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CONTENTS

THE INFLUENCE OF A MAGNETIC FIELD ON THE DIELECTRIC CONSTANTS OF GASEOUS AND LIQUID NITROGEN AND OXYGEN[1]

BY ALLAN C. YOUNG[2]

Abstract

The results of an experimental determination of the effect of a magnetic field on the dielectric constants of gaseous and liquid oxygen and nitrogen are given. With the gases a balanced resonance method was used, and with the liquids, a special bridge. The only positive result obtained was with gaseous oxygen at a pressure of 100 atm., and this can be accounted for quantitatively by the increased pressure of the oxygen in the magnetic field.

Introduction

The effect of a magnetic field on the dielectric constant, or more exactly the electric susceptibility of gases, is a problem of considerable interest, in the classical theory and new quantum mechanics, on account of its relation to the anisotropy of the molecules, and, in the old quantum theory, as a test of the validity of the spatial quantization of the angular momentum of the molecule in an applied field. The magnitude of the effect on the classical theory has been calculated by Weigle (9) and Van Vleck (4, 5, 6), and that on the old quantum theory by Pauling. The calculation of the effect on the new quantum mechanics has been attempted by Niessen (2), but his results hold only for a very specialized type of molecule which apparently has little physical significance. His results for this type of molecule agree in order of magnitude with calculations according to classical theory. More exact calculations have not been made, owing to mathematical difficulties and lack of experimental data. A complete outline of the problem and its theoretical significance is given by Van Vleck.

Several investigators, notably Weatherby and Wolf (8), Mott-Smith and Daily (1), Pützer (3), and Voss (7), have studied experimentally the effect of a magnetic field on the dielectric constant of gases. They found that within their limit of error, which in the case of Pützer and Voss was about one part in ten million, and more for the others, a magnetic field had no effect on the dielectric constant.

Weatherby and Wolf used a heterodyne method to measure the capacity change. They counted the number of beats produced per second between two oscillators, one with a fixed frequency and the other having a test con-

denser filled with the gas under test in its load circuit. They estimate that they can measure a frequency change of one cycle per second, which with their apparatus corresponds to a capacity change of one part in five hundred thousand. Mott-Smith and Daily used a similar method but measured their capacity change by observation of the change in the Lissajous figures produced by the superposition of the frequencies of the two oscillators. They estimate that they can detect a capacity change of one part in a hundred thousand. Pützer, using a method fundamentally the same as the latter, claims a sensitivity 100 times as great as that reported by Mott-Smith and Daily. In the apparatus used by Voss a test condenser formed part of a resonant circuit excited by a vacuum tube oscillator. The capacity and inductance values in the resonant circuit were adjusted to give the maximum current change in the resonant circuit for a given small capacity change. This current was passed through a thermocouple and the resulting direct current balanced against the current from another thermocouple also coupled to the oscillator. Since the calibrations of the two thermocouples were nearly the same, small changes in the oscillator intensity should not have affected the balance. The change of the balance current gave a measure of the change of capacity in the test circuit. For small capacity changes, the current change was directly proportional to the capacity change; with a very sensitive galvanometer in his balance circuit, Voss claims to have been able to detect capacity changes of one part in a hundred million. He did not, however, give this figure as his final limit of error, nor did he calibrate his apparatus in units of this order.

All these methods have one serious disadvantage, inasmuch as they depend on the condition that there be no circuit variations other than capacity change. The frequency stability of any ordinary oscillator is not much better than one part in a hundred thousand for a carefully designed oscillator. The frequency variations are probably due mainly to battery changes and surface charges on the glass of the vacuum tubes. In Voss's method this could be overcome by using a quartz crystal oscillator which has a possible deviation of one part in a million, or even in ten million for a circuit with thermostatic control. Temperature changes in the condenser itself constitute another source of error; changes of one-tenth of a degree cause a change of capacity of about one part in a million. A third source of error is the change of pressure of the gas in a magnetic field, an effect that depends on the magnetic susceptibility of the gas.

Experimental

In the present investigation both the heterodyne method and a modification of Voss's method were tried with gases. The detectable capacity change with the heterodyne method was found to be about one part in a hundred thousand; with the resonance method, about one-tenth of this. Hence, the modification of Voss's method shown in Fig. 1 was adopted for use with gases at high pressure. The vacuum tubes in the balance circuit were 8 ft. from the magnet, and were not appreciably affected by the magnetic field. Details of the layout and the test condenser are given in Figs. 2 and 3.
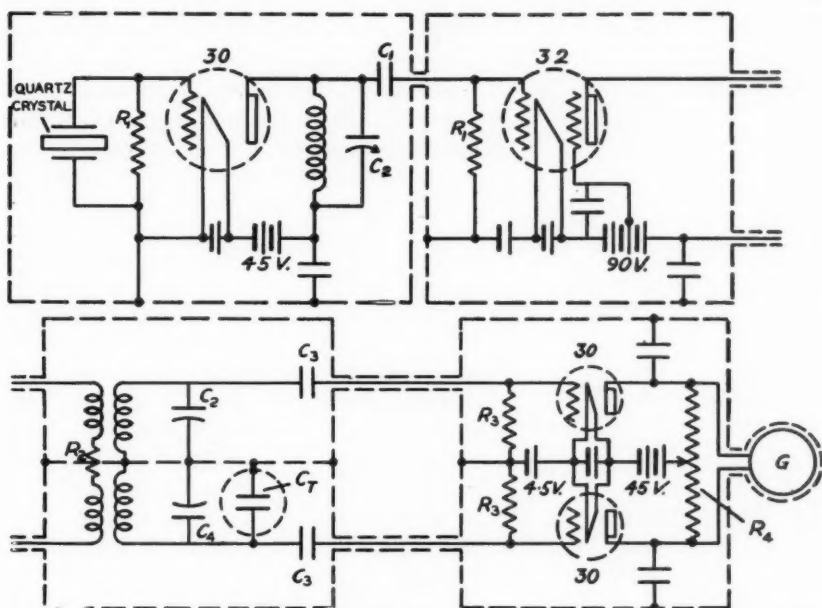
FIG. 1. *Variation of Voss's method for dielectric constant.* $R_1 = 2$ *megohms,* $R_2 = 50,000$ *ohms,* $R_3 = 1$ *megohm,* $R_4 = 10,000$ *ohm potentiometer,* $C_1 = 20$ *μμf.,* $C_2 = 50$ *μμf. max. V.C.,* $C_3 = 10$ *μμf. max. V.C.,* $C_4 = 2.5$ *μμf. max. V.C., with a calibration of* 3.5×10^{-4} *μμf. per scale division,* $C_T =$ *test condenser. All by-pass condensers are 0.1 μf.* $G =$ *galvanometer.*
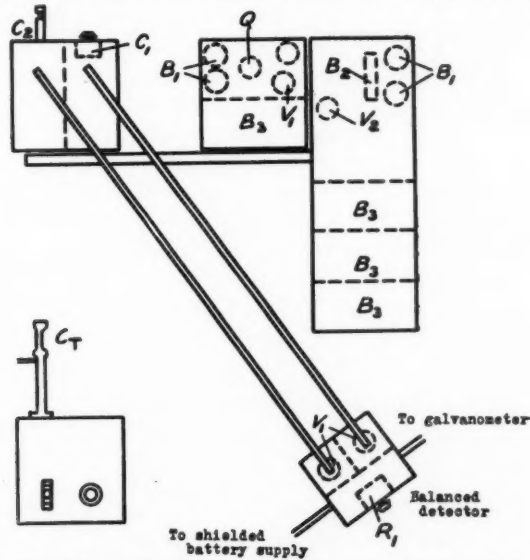
FIG. 2. *Actual layout of apparatus in 1.* $B_1 = 1.5$ *volt dry cell,* $B_2 = 4.5$ *volt dry battery,* $B_3 = 45$ *volt dry battery,* $C_1 = 50$ *μμf. max V.C.,* $C_2 = 2.5$ *uuf. max. V.C.,* $C_T =$ *test condenser,* $Q =$ *quartz crystal,* $R_1 = 10,000$ *ohm wire-wound potentiometer,* $V_1 =$ *Type 30 tube,* $V_2 =$ *Type 32 tube.*
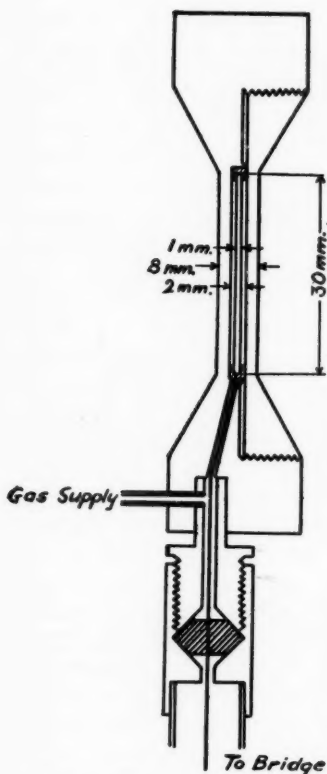
FIG. 3.   *Detail diagram of test condenser for gases.*

The plate current of the vacuum tubes could be balanced to 10^{-9} amp. with no high frequency voltage on the grid, but only to 10^{-8} amp. when the circuit was used with the high-frequency voltage applied to the grids. With this circuit a change of one scale division on the vernier condenser, corresponding to a capacity change of 3.5×10^{-4} $\mu\mu$f., caused a current of 1.8×10^{-7} amp. to flow through the galvanometer. This places a limit of 2.0×10^{-5} $\mu\mu$f. on the detectable capacity change. With the test condenser used, which had a capacity of 25 $\mu\mu$f., the minimum observable change in dielectric constant would be one part in 1.2×10^6. This method was not satisfactory for use with liquid oxygen or nitrogen, chiefly because of variations in capacity caused by temperature changes in the leads to the condenser.

For this reason the circuit used with liquids was a specially designed bridge in which variations due to temperature changes were nearly eliminated (Fig. 4). The practicable sensitivity of this bridge was less than that of the previous apparatus at room temperatures, but with liquids at low temperature the sensitivity was greater. With liquid oxygen and nitrogen in the condensers, a change of capacity of one part in a hundred thousand could be measured.

The bridge circuit can be considered as consisting of three distinct units, the feeding circuits, the bridge proper and the null indicator for determining the balance of the bridge. The feeding circuit consisted of a crystal oscillator (frequency 2.1 megacycles per second) and an amplifier connected to the input transformer of the bridge. The primary and secondary of the input transformer were shielded electrostatically from each other. The layout of the apparatus is shown in Fig. 5.

The bridge proper is made as symmetrical as possible in all respects. Two arms of the bridge consist of 50-$\mu\mu$f. maximum variable air condensers enclosed in a heavy copper shield connected to one side of each condenser. This shield prevents any variation of the capacity of the two condensers to ground when they are being adjusted. The other two arms of the bridge are condensers containing the liquid to be measured and a 200,000 ohm variable resistance. As may be seen from the diagram (Fig. 4) the input coil may also be considered as part of these arms, and any dissymmetry in
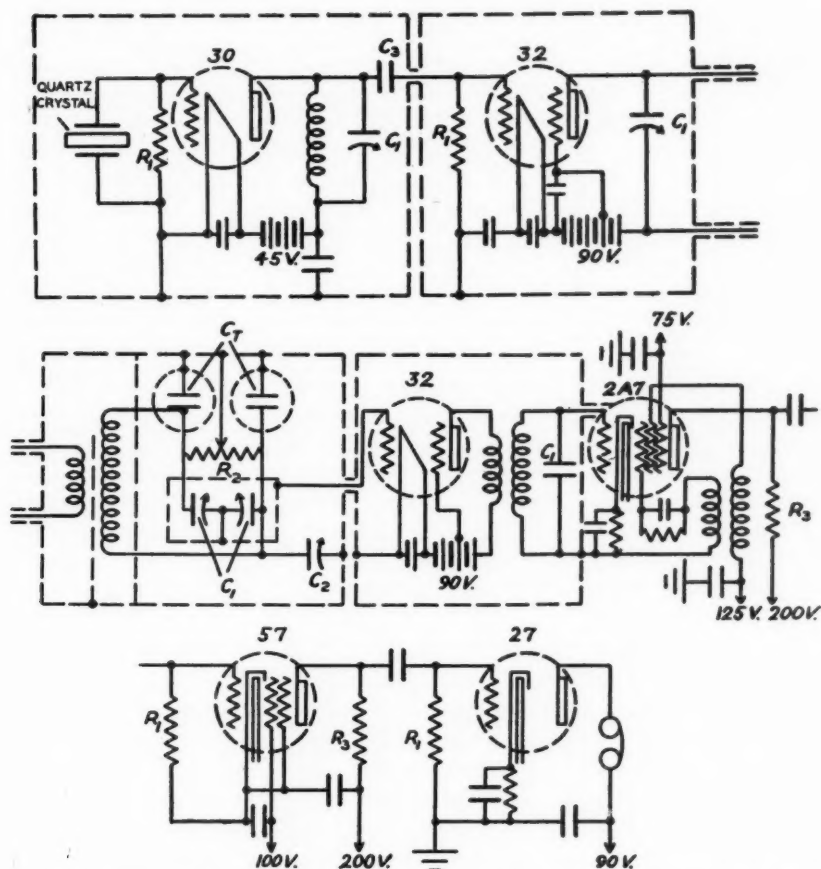
FIG. 4. *Diagram of apparatus used for the investigation of the effect of a magnetic field on the dielectric constants of liquid oxygen and nitrogen. $R_1 = 2$ megohms, $R_2 = 200,000$ ohm wire-wound potentiometer, $R_3 = 100,000$ ohms, $C_1 = 50$ μμf. max. V.C., $C_2 = 2.5$ μμf. max. V.C. calibration of 3.5×10^{-4} μμf. per scale division, $C_3 = 20$ μμf., $C_T = $ test condenser. All by-pass condensers are 0.1 μf.*

it will affect the resistance balance of the two arms. The variable resistance is adjusted to balance these resistances and any others that may be present owing to the resistance of the leads and dielectric losses. The design of the test condensers is shown in Fig. 6. The plates are made as nearly as possible identical. The double-walled container is designed to prevent any bending of the inner container by pressure effects developed by the magnetic field. A small variable condenser is connected in parallel with one of these condensers, and is used for the final balancing of the bridge and for measuring any change of dielectric constant.
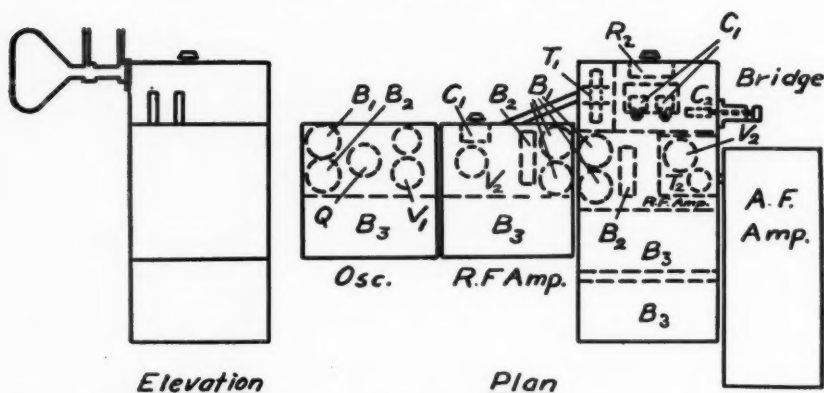
FIG. 5.   *Layout of apparatus in Fig. 4. B_1 = 1.5 volt dry cell, B_2 = 4.5 volt dry battery, B_3 = 45 volt dry battery, C_1 = 50 $\mu\mu f.$ max. V.C., C_2 = 2.5 $\mu\mu f.$ max. V.C., R_2 = 200,000 ohm wire-wound potentiometer, T_1 = input transformer to the bridge, T_2 = output transformer to the converter tube, V_1 = Type 30 tube, V_2 = Type 32 tube, Q = quartz crystal.*
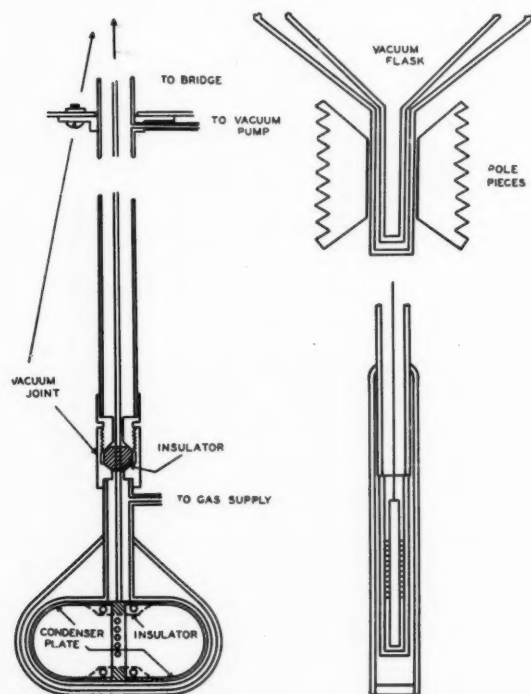
FIG. 6.   *Detail diagram of vacuum flask condenser for liquids.*

The output circuit is connected to the shield of the two variable condensers and to ground, which is the common point of the two fixed condensers. The current from the bridge is passed through a one stage, shielded, high-frequency amplifier to a converter tube. In this tube the current from the bridge is mixed with a current of slightly different frequency generated in the converter tube. These two currents combine to give in the output of the tube a current whose frequency is the difference of frequencies generated by the crystal oscillator and converter tube. This current, which has a frequency of a few thousand cycles per second, is further amplified and then fed to a pair of earphones. This method was adopted as it is more sensitive for small currents (*i.e.*, when the bridge is near balance) than the more customary method of modulating the oscillator output and using an audio frequency amplifier as a balance detector.

The test condenser and its replica are mounted in a specially made German silver Dewar flask. This flask has an external width of only 13 mm. in the vicinity of the test condenser. This permits the placing of the pole pieces of the magnet less than 15 mm. apart. The magnet is a standard Boas electromagnet which, with a current of 22 amp., has a field strength of 19,000 gauss over an area of 7 sq. cm. when the gap is 15 mm. The field strength was measured with a bismuth spiral. Both types of apparatus were tested by observing the effect of the magnetic field when the test condensers were evacuated to a pressure of 0.01 mm. of mercury. No effect was observed within the stated limits of error.

All previous workers have used gases at atmospheric pressure or less. However, classical theory predicts that the electrical susceptibility, χ, of a gas in a magnetic field, H, will be (6, p. 117)

$$\chi = N(a + bH^2)$$
$$= \chi_o(1 + b/aH^2) ,$$

where N is the number of molecules per cc.

$$a = \frac{\mu_1^2 + \mu_2^2 + \mu_3^2}{3kT} + \frac{\alpha_{11} + \alpha_{22} + \alpha_{33}}{3}$$

$$b = \frac{3\cos^2\Psi - 1}{90k^2T^2} \sum_{i>j} \left[(\mu_i^{*2} - \mu_j^{*2})\left(\frac{\mu_i^2 - \mu_j^2}{kT} + \alpha_{ii} - \alpha_{jj}\right) + 6\mu_i^* \mu_j^* \left(\frac{\mu_i \mu_j}{kT} + \alpha_{ij}\right)\right],$$

where μ_1, μ_2, μ_3 are the components of permanent electric moment of the molecule, μ_1^*, μ_2^*, μ_3^* are the components of permanent magnetic moment of the molecule, α_{ij} are the polarization coefficients and are a measure of the distortion of the molecule by an applied electric field; i and j can take the values 1, 2, 3. ψ is the angle between the applied electric and magnetic fields.

From this it follows that the dielectric constant, ϵ, is given by:

$$\epsilon = 1 + 4\pi\chi_o(1 + bH^2/a) .$$

Therefore $\frac{\Delta\epsilon}{\epsilon_o} \doteq cH^2\{\chi_o/(1 + 4\pi\chi_o)\}/T^2$, where $\Delta\epsilon = \epsilon_H - \epsilon_o$, 　　(1)

since the μ's are all zero, as oxygen and nitrogen are non-polar (*cf.* Van Vleck (4,5,6)).

Using this classical result as a guide, it follows that the percentage change in dielectric constant, for a given magnetic field, will be increased by an increase in χ_0 and a decrease in temperature. Hence measurements of the effect of a magnetic field on the dielectric constant of oxygen and nitrogen were made under the following conditions:

1. At 100 atm. pressure and room temperature.

2. In the liquid state at the temperature of liquid air under atmospheric pressure.

While these conditions are such that Equation (1) would not be expected to hold exactly, nevertheless it is unlikely that the order of magnitude of the effect would be changed.

Results

In the preliminary work, in which a method similar to that employed by Voss was used, an apparent increase of the dielectric constant of oxygen gas at 100 atm. pressure and room temperature was observed. The balance current changed by 1.4×10^{-8} amp., which corresponds to a change of 1.1×10^{-6} in the dielectric constant. With nitrogen gas under similar conditions no effect was observed. The change in the capacity however may be attributed to the pressure change in the gas in the condenser due to the applied field. If K is the volume-magnetic susceptibility of the gas, the pressure increase will be:

$$\Delta p = KH^2/2 \; ;$$

for oxygen at 20° C. and 100 atm.

$$K = 1.4 \times 10^{-5}$$
$$\therefore \Delta p = 1.9 \text{ mm. of mercury.}$$

Since the dielectric constant of oxygen at 20° C. and one atmosphere is 1.00051, the change in dielectric constant will be

$$\Delta \epsilon = 1.3 \times 10^{-6} \; .$$

This is the value observed, within experimental error. The magnitude of the magnetic susceptibility of nitrogen is only $\frac{1}{300}$ that of oxygen, hence no effect is to be expected due to pressure changes. Since the compressibility of liquids is much less than that of gases, this magnetic effect will not introduce errors of so large a magnitude in the measurements of their electric susceptibilities. Based on calculations similar to the above, the change in the dielectric constant of liquid oxygen is approximately one part in a million for a field of 20,000 gauss.

With the bridge previously described no change was observed in the dielectric constant of liquid oxygen or nitrogen in fields as strong as 19,000 gauss. Since the only effect observed is that on oxygen gas at high pressure and in strong magnetic fields, and since this effect may be accounted for by the increase of pressure of the gas in the magnetic field, it may be concluded that any effect of magnetic field on the dielectric constant is at least as small as that indicated by rough calculations based on the classical theory. Further

it may be concluded that any effect on oxygen at least will be masked by the presence of magnetostrictive effects which, with apparatus of the type described, cannot be calculated exactly owing to field inhomogeneities.

TABLE I

LIMIT OF ERROR IN WORK BY PREVIOUS INVESTIGATORS

Gas	Author	$\Delta\epsilon/\epsilon$	$\Delta\chi/\chi$	$T^2\Delta\chi/H^2\chi$
He	Weatherby and Wolf	2×10^{-6}	1×10^{-1}	1×10^{-4}
O_2	Weatherby and Wolf	2×10^{-6}	4×10^{-3}	5×10^{-6}
NO	Mott-Smith and Daily	1×10^{-5}	8×10^{-2}	3×10^{-4}
HCl	Mott-Smith and Daily	1×10^{-5}	1×10^{-2}	3×10^{-5}
N_2	Pützer	1×10^{-7}	2×10^{-4}	2×10^{-7}
O_2	Pützer	1×10^{-7}	2×10^{-4}	2×10^{-7}
O_2	Voss	3×10^{-7}	1×10^{-2}	1×10^{-4}
A	Voss	5×10^{-7}	1×10^{-2}	7×10^{-5}
O_2	Young	1×10^{-6}	2×10^{-3}	4×10^{-9}
N_2	Young	1×10^{-6}	2×10^{-5}	4×10^{-9}
O_2 (liquid)	Young	1×10^{-6}	3×10^{-5}	6×10^{-10}
N_2 (liquid)	Young	1×10^{-5}	3×10^{-5}	6×10^{-10}

Acknowledgments

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120

STUDIES ON EXPLOSIVE ANTIMONY

III. THE MAGNETIC SUSCEPTIBILITY[1]

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Abstract

Explosive antimony is not as diamagnetic as the ordinary polycrystalline metal. The magnetic susceptibilities are respectively -0.38×10^{-6} and -0.88×10^{-6}. The explosive or amorphous form should therefore be regarded as a true glass of the supercooled liquid. The fact that it is less "metallic" than the molten metal cannot be the result of the metallic binding of the liquid or crystalline state changing to homopolar binding in the amorphous state.

Introduction

The data presented in Parts I (4) and II (3) of this series indicate that explosive antimony is amorphous, and that its "explosion" is a crystallization. The properties of this unstable electrolytic deposit are being studied in the hope that they may throw some light on the problem of amorphous metals in general. It seems probable that no other metal can be obtained in the amorphous state so easily and in such quantities.

Measurements of the magnetic susceptibility were undertaken with the object of determining the type of atomic binding characteristic of the amorphous metal. Ordinary crystalline antimony and bismuth are diamagnetic because of the presence of homopolar bonds. The disappearance of these bonds when the crystal melts is accompanied by a decrease in diamagnetism and electrical resistance, so that the liquid is more truly a metal than is the solid. If explosive antimony is amorphous in the sense that it is a glass of supercooled liquid, it should therefore be less diamagnetic than ordinary antimony.

On the other hand, the electrical properties indicate that explosive antimony is far less metallic than crystalline antimony (3). If this loss of metallic properties is the result of the replacement of metallic by homopolar binding, explosive antimony should be even more diamagnetic than the crystalline variety. Bernal has pointed out that the structure of the latter can be pictured as a layer lattice in which the bonds between the atoms of a layer are homopolar, and those between the layers are metallic (1, p. 375). In keeping with this view is the fact that crystalline antimony has a higher conductivity across than in the cleavage plane, and shows directional abnormalities in the conductivity at high pressures (2, p. 274). In explosive antimony, cleavage planes and, to a large extent, metallic properties have disappeared, so that it seems not unreasonable to suspect that the metallic bonds of the ordinary metal have become homopolar in the amorphous form.

The determination of the magnetic susceptibility of the explosive deposit offers an obvious means of choosing between these two possibilities. It may be stated at once that the amorphous metal is much less diamagnetic than the polycrystalline metal, so that in all probability the former is a true glass of the supercooled liquid.

Experimental

Preparation of Specimens

Fairly large cylindrical specimens of uniform composition and cross section were required for the magnetic susceptibility measurements, which were made by a modified Gouy method. As the material cannot be machined without explosion the specimens used were untouched electrolytic deposits. It has been already shown (4, 5) that the chemical and physical uniformity of an explosive cathode depends largely upon the efficiency with which the bath is stirred during the deposition. A poorly stirred bath will yield rough and misshapen cathodes which often consist of a mixture of the explosive and non-explosive forms. Such deposits are coarsely botryoidal in structure and have little or no metallic lustre. High speed stirring, on the other hand, results in symmetrical deposits of uniform chemical composition. If a cathode be rapidly rotated about its own axis in a well stirred bath, the finished product will generally resemble a rod of highly polished steel.

The stirring arrangement shown in Fig. 1 proved to be very satisfactory. A large gear, A, 9 cm. in diameter, is fixed to the stationary shaft, B, which supports the whole mechanism. A small gear, C, is carried on either end of the bar D which is fixed to the driving pulley, F, by a hollow shaft, H. The copper wire cathodes are held in chucks attached to the gears, C, which mesh with A and therefore rotate about their own axis as they revolve with D. The gear ratios are such that the smaller two make five revolutions about their own axis for every revolution about A. The cross bar, D, was turned at the rate of 300 r.p.m. The anode of cast chemically pure antimony was mounted at the centre of the electrolysis cell as shown in the figure. The electrolyte was redistilled chemically pure antimony trichloride dissolved in 10% hydrochloric acid solution. Precautions were taken to avoid contamination by iron.
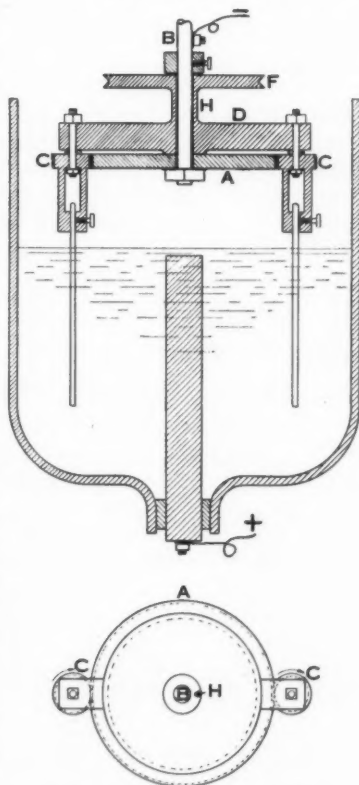
Fig. 1. *Details of cathode-stirrer.*

Although very uniform specimens could be prepared with this apparatus, it proved to be unexpectedly difficult to make them very large.   On attaining a certain size (less than 1 cm. in diameter) the cathodes usually exploded in the bath unless the current density was kept so low that the deposition proceeded at an inconveniently slow rate.   The explanation of these explosions is probably to be found in the fact that the amorphous metal has a very high resistance (4), which at high current densities might lead to local heating above the temperature (about 100° C.) at which the crystallization becomes explosive.   After many attempts three suitable specimens were obtained in non-stop runs of 30 to 40 hr. duration.

Magnetic Susceptibility Measurements

The specimen was carried in a light, close-fitting test tube suspended by a fine copper wire from the beam of an analytical balance, which stood on a firm support about two feet above the flat-faced pole pieces of a large electromagnet.   The length of the copper wire was such that the lower end of the specimen was about 1 cm. below the top of the pole pieces, which were spaced with hardwood blocks to form a gap not more than 1 mm. greater than the diameter of the glass tube.   The susceptibility of a specimen was determined by comparing the apparent change in weight caused by the field with the change that the same field produced in the apparent weight of the glass tube filled with distilled water.   Corrections must be made for the diamagnetism of the glass and of the copper wire (the cathode basis metal) embedded in the antimony specimen, as well as for the fact that the cross section of the water column is necessarily greater than that of the antimony. The method of making these corrections will be clear from the following sample calculation.   The density of explosive antimony is taken as 6.8 and the magnetic susceptibility of water as -0.72×10^{-6}.

Sample Calculation

Experiment 12, Specimen 3.   Temperature 25–27° C.

	Current in magnet, amp.	Weight (W), gm.	ΔW
Glass tube + copper wire	0	4.5442	
	3.000	4.5402	−0.0040
Glass tube + specimen	0	29.1433	
	3.000	29.0484	−0.0949
Glass tube + specimen + water	0	32.5274	
	3.000	32.4175	−0.1099
Glass tube + copper wire + water	0	12.1619	
	3.000	12.1038	−0.0581

$$\Delta W_{Sb} + \Delta W_z = -0.1099 - (-0.0040) = -0.1059$$
$$\Delta W_{Sb} - \Delta W_z = -0.0949 - (-0.0040) = -0.0909$$

$$2\Delta W_z = -0.0150$$
$$\Delta W_z = -0.0075$$
$$\Delta W_{Sb} = -0.1059 - (-0.0075) = -0.0984$$

$$\Delta W_{H_2O} + \Delta W_z = -0.0581 - (-0.0040) = -0.0541$$
$$\Delta W_{H_2O} = -0.0541 - (-0.0075) = -0.0466$$

COFFIN: STUDIES ON EXPLOSIVE ANTIMONY123

Therefore, for explosive antimony,

$$\chi = \frac{-0.72 \times 10^{-6} \times -0.0984}{-0.0466 \times 6.8} = -0.22 \times 10^{-6}.$$

In the foregoing calculation ΔW_z is the apparent change in weight of the water layer between the cylinder of antimony and the wall of the glass tube. Although the values obtained for different specimens did not agree particularly well, the susceptibility of any one specimen could be checked from day to day to well within 0.5%. The magnetic susceptibility of purified benzene was found to be -0.714×10^{-6}, in excellent agreement with the value 0.712×10^{-6} given in the International Critical Tables.

After determining the susceptibility of an explosive specimen, it was crystallized non-explosively by keeping it for 24 hr. at 80° C. and then 24 hr. at 110° C. (4). Its magnetic susceptibility was then redetermined. All measurements on the explosive deposits were made within a few days of their preparation, so that no appreciable crystallization could have occurred (3).

Discussion of Results

The three specimens of explosive antimony used for these measurements are described in Table I.

TABLE I

SPECIMENS OF EXPLOSIVE ANTIMONY USED FOR MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Specimen No.	Wt. Sb., gm.	% SbCl$_3$ in sol'n.	% SbCl$_3$ in metal	Approx. length, cm.	Approx. diam., cm.
1	34.84	15	5	6.5	1
2	13.85	31	6	6	0.3
3	24.53	31	6	6	0.9

Column 4 gives the approximate percentage of antimony trichloride in the metal, as interpolated from the antimony trichloride concentration of the solution (column 3) from which it was deposited (6). Specimens 2 and 3 were very bright and smooth and of uniform diameter. Specimen 1 was bright but was somewhat rough and uncylindrical. The results of the magnetic susceptibility measurements are given in Table II. The results of all determinations are listed.

TABLE II

THE MAGNETIC SUSCEPTIBILITY OF EXPLOSIVE AND OF CRYSTALLINE ANTIMONY

Specimen	$\chi \times 10^6$	Mean $\chi \times 10^6$
No. 1 Explosive	$-0.21, -0.21$	-0.21
No. 1 Crystallized	$-0.42, -0.41$	-0.42
No. 2 Explosive	$-0.19, -0.19$	-0.19
No. 2 Crystallized	$-0.44, -0.44$	-0.44
No. 3 Explosive	$-0.22, -0.22, -0.22$	-0.22
No. 3 Crystallized	$-0.52, -0.49, -0.49$	-0.50

Mean value of χ for amorphous antimony $= -0.21 \times 10^{-6}$
Mean value of χ for crystallized antimony $= -0.45 \times 10^{-6}$

There is a small correction to be made for the diamagnetism of the antimony trichloride ($\chi = -0.36 \times 10^{-6}$) present in these specimens. The assumption that there is 5% of antimony trichloride as such in both the amorphous and crystalline metal changes the values in Table II for the susceptibilities by about $+0.01 \times 10^{-6}$ and -0.01×10^{-6} respectively. These values thus become

$$\chi(\text{explosive Sb}) = -0.20 \times 10^{-6}$$
$$\chi(\text{crystallized Sb}) = -0.46 \times 10^{-6}$$

The I.C.T. give $\chi(\text{crystalline Sb}) = -0.87 \times 10^{-6}$.

This discrepancy between the magnetic susceptibility observed for the crystallized specimens and that given in the literature for the polycrystalline metal is probably due to the presence of traces of iron in the electrolytic preparations. The great difficulty in avoiding or correcting for traces of ferromagnetic material in work of this kind is well known (10, p. 505), and it seems fairly certain that iron dissolved in antimony is in a ferromagnetic state (8, p. 373).

As a test of the magnetic purity of the starting material, two polycrystalline rods were cast from the same "chemically pure" antimony that had been used for the anodes in the preparation of the explosive specimens, and their susceptibilities were measured. The value found, viz., -0.54×10^{-6}, is much closer to that of the crystallized specimens than to that given in the literature. It thus seems probable that the presence of iron is the cause of the low diamagnetism of the crystallized material, and that both the amorphous and the crystallized metal are more diamagnetic than the foregoing experiments indicate. If this assumption is correct, the true value for the magnetic susceptibility of amorphous antimony is probably about -0.38×10^{-6}. The amorphous metal is thus somewhat less diamagnetic than even liquid antimony at the melting point ($\chi = -0.49 \times 10^{-6}$). The values are nearly enough alike, however, to suggest that the internal binding is very much the same in the two cases, and that some mechanism other than the disappearance of metallic bonds must account for the loss of metallic properties that occurs when the metal becomes amorphous. The high resistance (at 0° C. about 100,000 times that of ordinary antimony (3)) and its negative temperature coefficient are properties of the material that are difficult to explain unless the disappearance of metallic bonds is assumed.

It has been recently suggested by Prins (9), who has also found explosive antimony to be less diamagnetic than ordinary antimony, that the high resistance of the explosive form is due to the presence of the antimony trichloride, which may exist as insulating films within the metal. In support of this view are the facts that the specific resistance increases with increasing antimony trichloride content, and that the material is distinctly heterogeneous (4). On the other hand, the fact that amorphous films of antimony containing no antimony trichloride show much the same peculiarities with regard to the electrical resistance and its temperature coefficient (7) is definitely opposed to this hypothesis.

Acknowledgment

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A NEW METHOD FOR THE APPLICATION OF LUMINESCENT SCREENS TO GLASS SURFACES[1]

By W. H. KOHL[2]

Abstract

An outline is given of the various methods for the application of luminescent screens, and their relative merits. Most widespread in use are methods that utilize a liquid binder that enters into a chemical reaction with the glass surface. In other cases, the powder is partially imbedded in the glass surface by a sintering process. The physical characteristics of the luminescent screen are adversely affected by both of these methods. A process based on the activation of the glass surface by a deposit of sulphur is described. The sulphur coating picks up the luminescent powder in a uniform layer when it is brought into contact with the powder. After being removed by means of a moderate heat treatment, it leaves the screen firmly adhering to the glass surface. Possible mechanisms for the process are briefly discussed.

History and Current Methods

The coating of glass surfaces with powders, and in particular the coating of the inside wall of a glass envelope, constitutes an important process in the manufacture of cathode ray tubes. In the early Braun tube (4) the luminescent screen was painted on a mica disc, which was held in position close to the inside of the face of the bulb. Viewed from the outside, the luminescent spot was necessarily of low intensity, owing to the absorption of light in the mica disc and in the glass wall. Varley (15), who worked with Braun in Strassbourg, therefore replaced the mica disc by a glass disc, and finally applied the screen directly to the inside wall of the tube.

In order to make the screen adhere to the glass surface, the powder was either mixed with sodium silicate (water glass) and painted on with a brush, or dusted on to a film of water glass and then sintered on to the glass by heat treatment. Screens made in this fashion are liable to show brush marks and are easily discolored or burnt when exposed to the electron beam. This is due to a reduction of the binder and its chemical reaction with the glass. Potassium water glass has lately been used to greater advantage as a binder in this method (1, pp. 85-88). L. M. Hull (8) used a lacquer binder instead of water glass.

Another method in wide use up to the present day is that developed by Everett and described by Sir J. J. Thomson (14). The powder is allowed to settle slowly from a suspension in alcohol. "When the deposit has reached the requisite thickness, the rest of the suspension is drawn off and the deposit allowed to dry; when dry it sticks quite firmly to the plate." Unless sintered into the glass, however, such screens are very sensitive to mechanical shocks, and therefore not suitable for shipment.

It is from another viewpoint that carbon compounds such as alcohol, acetone, ethyl oxalate, glycerine, and others, are not suitable as binders for screen

materials.   It has been observed throughout the development of the Braun tube that such screens are liable to build up surface layers, which are apt to block the electron stream and prevent it from hitting the fluorescent material proper (1, 15).   The phenomenon observed is the emanation, from the centre of a dark circular area around the point of impact of the beam as centre, of fluorescent streamers that travel towards the edge of the screen where the electrons, which glide over the charged surface, are able to excite the outer regions to fluorescence.   Stewart (11) has given an account of the formation of insulating films caused by electron and ion bombardment in the presence of the slightest traces of organic vapors in an evacuated tube ($p = 10^{-5}$ mm. of mercury) for electron velocities in the range 190 to 210 volts.   Stewart points out that these films are formed only at the point of impact of the rays on the surface, and may be attributed to carbon compounds formed by the polymerization of organic vapors.   They are formed on glass and metal surfaces that are exposed to bombardment by the particles in question.

Black circular areas on the lower side of an anode disc with the aperture as centre and interference fringes at the edge were repeatedly observed by the author during the earlier stages of the development of cathode ray tubes. In each of these cases the screen was put on with an organic binder.

The exclusion of such binders is essential for the reasons given above. The only alternative method left for the application of luminescent screens seems to be that of Espe (6; 1, p. 86).   The glass surface is wetted with distilled water and the fine powder dusted onto it so as to form a uniform layer.   The blank is then heated to a temperature near the softening point of the glass, so that the powder particles sink into the glass and are firmly imbedded in it after the glass has cooled down.   Particles not in firm contact with the glass may then be removed with a brush.   Such screens have the appearance of frosted glass and withstand the bombardment by a high energy beam better than others, owing to the high heat conductivity of the imbedded screen particles.   This may be further increased by admixing with the powder a glass dust of a low melting point.   Plots of the luminous intensity of the fluorescent spot as a function of the energy input are given by Ardenne (1, pp. 85-88) for a screen of $CaWO_4$ prepared with a potassium silicate binder in one case, and without any binder, but sintered only, in the other.   The plots disclose a superior and almost linear characteristic for the sintered screen.

Unfortunately, the luminous intensity of the spot on the screen is partly dissipated in the glass wall and forms a "halo" or "spurious rings" around the spot proper.   Hughes (7) and v. Ardenne (2, 3) have studied the causes of the formation of this halo, and the latter suggested means for its reduction. Assuming a perfectly concentrated electron beam exciting fluorescence in one particle of the screen surface, it is found that the halo is due to total reflection of the fluorescent radiation at the glass-air interface of the glass wall.   The radius of the halo will be approximately twice the thickness of the wall.   Furthermore, it will be larger for a screen particle that is partly imbedded in the glass wall by the sintering process than for a particle that is but loosely bound

to the surface by a binder and has a smaller contact area with the glass. Photometric measurements of the relative intensity of the halo with respect to the total brightness of the luminescent radiation disclose that 25 to 28% of the total luminescent radiation is dissipated in the halo in a sintered screen and only $1\frac{1}{2}$ to 4% in a loosely bound screen.   The reduction of the diameter and the intensity of the halo is of great importance for the perfection of television images, as well as for obtaining sharp oscillographic curves.   It requires the development of special binders of low absorption coefficients and special chemical characteristics.   Many workers in the field strive towards this end, and the results obtained are generally guarded with great care.   A method that would combine the advantage of a loosely bound screen with the absence of a physical binder, seems to be an ideal solution of the problem.

During a number of years spent on the development of cathode ray tubes, the author encountered in the preparation of fluorescent screens all the difficulties that are described above in part.   Suspensions of the powder in acetone and in amyl acetate, which were sprayed on to the glass wall, gave smooth screen surfaces that responded well to the electron beam for a short time, but showed marked deterioration of brilliancy and charge effects, even in gas filled tubes, after a day or so.   It was at this stage that a fundamentally different method, one that did not involve the use of organic binders, was sought.

Description of New Method

H. W. Parker* observed that a condensate (obtained by burning sulphur in air) on the glass wall easily picked up the powder in a thin and uniform layer when the powder was put into the bulb, and the bulb revolved over a sharp flame.   A uniform sintered screen that could not easily be removed from the glass was thus formed.

A further investigation of the possibilities of sulphur as a binder was suggested to the author and led to the following process, which was developed during the summer of 1933, and has been in use in this laboratory ever since, with only slight modifications.

Experimental tests of electrode structures, cathode designs and luminescent materials are for economic reasons generally carried out with small tubes. Radio tube blanks are useful for this purpose.   The application of screens to the face of such envelopes will be described first.

Coating of Small Blanks

A small glass container (10 cc.) is filled with carbon disulphide† and heated electrically so that the liquid boils quietly (b.p. 46° C.).   When lit with a match, the vapor burns with a light blue flame about two inches long.   The

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Chief Engineer of Rogers Radio Tubes Limited.

†*Carbon disulphide is a volatile liquid and poisonous.   Its vapor pressure at 1 atm. is 300 mm. of mercury.   The vapor forms an explosive mixture with air.   It should, therefore, be handled with care.*

blank to be coated is carefully cleaned and held over the flame so as to partially cover it. The products of the chemical reaction are carbon dioxide, sulphur dioxide, sulphur trioxide, and sulphur due to incomplete combustion. Sulphur trioxide is formed to a small extent in the presence of water vapor. For the purpose of the present description of the technical features of the process, it will be assumed that sulphur vapor is the main product of the reaction. A few seconds after the blank is exposed to the vapor stream, a deposit forms suddenly on the glass wall and gradually becomes heavier. The blank is filled with a dense cloud. When the deposit is of a yellowish green color, the blank is removed from the flame and allowed to cool. The deposit is then wiped from the wall of the blank with a cloth, except for the part that is to carry the screen. The fluorescent powder, which must be in a free flowing state, *i.e.*, dry and of uniformly small particle size, is put into the blank and brought into contact with the sulphur coating by shaking it quickly with a circular motion. The sulphur coating picks up a uniform thickness of powder that is determined by the thickness of the original coating. The excess powder is removed by turning the blank upside down and shaking it violently. The wall is then wiped clean with a cloth and the edge of the screen reduced to the desired diameter. The sulphur deposit on the screen is driven off by holding the blank over a Bunsen flame of moderate temperature for a few minutes. This completes the process. A perfectly uniform screen adheres to the surface of the glass. The screen cannot be shaken off after exhaustion of the tube, but it can easily be removed with a cloth if another screen is to be put on. Blanks of medium size (3 in. screen diameter) can be coated in the same way. While exposing the blank to the vapor it is advisable to rotate it slowly in a holder, to ensure a uniform deposit of the vapor on the screen surface. The coating of such small blanks is carried out very easily in a very short time and at a minimum cost. The excess powder from the coating of one blank can immediately be used for the next one.

Coating of Large Blanks

Large-sized blanks for cathode ray tubes of 5 in. or greater screen diameter require a specially designed double wall chimney that guides the vapor towards the screen surface, and prevents its condensation on the neck of the tube. This funnel ends in a specially designed mouthpiece which has a hollow glass cone with its apex pointing downwards, and which is supported in the inner tube. It serves to distribute the rising stream of vapor over a spherical angle and prevents it from hitting the centre of the screen surface directly. The blank is rotated slowly during this stage of the process; after about 10 min. a heavy deposit of sulphur is obtained. It was found useful, though not necessary, to cool the surface by means of water in a cylindrical container that fitted tightly over the face of the blank and rotated with it. After it has circulated within the bulb, the vapor is pumped off through the funnel by means of a water jet pump. This protects the operator from escaping sulphur vapors. The blank is then cleaned with a cloth, with which the

sulphur deposit may be easily removed from the wall. In order to obtain a uniform screen, the powder should be whirled into a cloud before it makes contact with the surface. If the powder makes its first contact with the screen in a mass, streaks are liable to be left, but after the original contact the powder is allowed to slide over the surface in bulk.

Physical Qualities of the Screen

The screen material is generally passed through a 200 mesh sieve to ensure approximately uniform particle size. The diameter of a particle was, therefore, on the average, of the order of 50 μ. Whether there exists an optimum particle size, as found by A. v. Buzágh (5) for microscopic particles in a liquid suspension adhering on surfaces which consist of the same material as the particles, has not been determined. When observed under a microscope, the completed screen appears as a fairly close packing of one layer of particles with interspaces on boundary lines unoccupied, owing to the irregular shape of individual particles. Here and there a larger particle rests on top of this layer. The screen has a transmittance approximately that of frosted glass, and appears white, gray, or whitish yellow, depending on the natural color of the screen material. Electrons penetrate only to about 10^{-4} cm. into the dielectric, as determined by the equation $d = KV^4$, where d is the depth of penetration, V is the volt equivalent of electron beam velocity, and K is a constant. For potentials commonly applied to cathode ray tubes, the depth of penetration is very small. A thin uniform screen is therefore most efficient.

Screens prepared in the manner described above are of high brilliancy, and show no deterioration other than that due to the quality of the screen material itself. They are equally suitable for gas filled and high vacuum type tubes. Their mechanical strength is not affected by the heat treatment of the tube necessary in the exhaustion process, during which the temperature is raised to 480° C. The tenacity with which the surface forces hold the powder is evident from the following simple tests. The screen cannot be separated from the glass by a strong stream of air, by any violent shocks, or by filling the tube with water and then drying it again over a flame. However, the coating can easily be wiped off with a cloth. This shows that the particles are loosely bound to the surface. Finished screens can be left exposed to the atmosphere for any length of time before being sealed and exhausted. Sulphur coated blanks may also be stored for days before the powder is applied. It is advisable, however, to complete the process without interruption.

Consideration of the Mechanism of the Process

No attempt will be made in this preliminary report to present a theory of the mechanism of this process. Lack of time and equipment has made quantitative measurements impossible so far. A closer study has recently been undertaken at the McLennan Institute of the University of Toronto.

A few observations will be reported, however, and possible correlations with other phenomena in the field of surface physics pointed out as a suggestion for further research.

A thin glass disc was moved slowly through a carbon disulphide flame and then observed under a microscope. A matrix of closely arranged tiny droplets covering the surface was thus formed. The disc was then moved through the flame again, observed, and this procedure repeated several times. On repeated exposures to the flame, the size of the globules gradually increased and the matrix became less dense, until finally several adjacent globules combined to form elongated, irregularly shaped bands, which were interlaced and looked like the pattern of a labyrinth. The formation of such droplets by the condensation of vapors on metal or glass surfaces is a well known phenomenon, and was recently studied carefully by Tammann and Boehme (13). They investigated the condensation of water vapor on metal and glass surfaces, and, with a microscope, counted the number of droplets per unit area. It was found that condensation centres exist on the surface, and that, after a deposit is removed with the aid of heat, repeated condensations lead to the formation of individual droplets at the same points on the surface. The number of droplets formed per unit area on different metals shows a correlation with their position in the Volta series. Condensation occurs most readily at crystal interfaces and where there are tool marks. The number of droplets formed on glass was only half that on gold (200 per 0.01 mm.^{2} on gold).

The activation of the glass surface by the sulphur deposit may be explained in one of the following ways:

1. The sulphur may act as a cleaning agent and allow the powder particle to come in contact with a clean surface after the evaporation of the droplet underneath, and be held by surface forces.

2. A very thin layer of amorphous sulphur might adhere to the surface even after the heat treatment, and act as a binder. This is considered to be unlikely, as the slightest traces of sulphur would tend to poison the cathode, and this would affect the thermionic emission. No such effect was ever observed.

3. The powder particles are undoubtedly charged electrically, owing to their mutual friction during the process of application. On the other hand, the glass surface is most probably charged during the exposure to the sulphur vapor, in a manner similar to that described by Stimson (12) for the building up of charges on hot metallic surfaces during the adsorption of gases. The role of the sulphur may then be to charge the glass surface and thus cause the binding of the powder by electrical forces.

To clarify this mechanism and ascertain whether other vapors would have a similar effect should prove to be an interesting study.

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HYDROGENATIONS IN A TETRALIN MEDIUM

I. DESTRUCTIVE HYDROGENATION OF BITUMEN AND PITCH[1]

BY E. H. BOOMER[2] AND J. EDWARDS[3]

Abstract

The importance of a suspension medium in processes of destructive hydrogenation is discussed, with particular reference to the efficiency of the medium as a hydrogen carrier. The value of tetralin as a medium, in that it is a good solvent, is stable to heat, and acts as a hydrogen carrier, has been determined in the hydrogenation of bitumen and stable pitch. Tetralin does not cause an increase in yield of oil but does improve the quality somewhat. It increases the rate of hydrogenation of bitumen but does not affect that of stable pitch.

Introduction

Previous reports from this laboratory (2, 3) on the destructive hydrogenation of coal have shown the importance of the suspension medium in such processes. Within the limits of the work, it was found that the medium was fully as important as any added solid catalyst. Consideration of the reactions involved suggests that such a result might be expected. As the term implies, destructive hydrogenation involves two principal reactions; namely, thermal decomposition and hydrogenation. Both reactions are concurrent and take place until substances resistant to further action are produced, but the reactions differ fundamentally in their basic characteristics (9). Thermal decomposition is irreversible and proceeds to completion, yielding gas and coke, the velocity of the reaction increasing rapidly with rising temperature. The reaction may be described as a monomolecular decomposition accompanied by polymerization of the products. In contrast, the hydrogenation reaction is reversible and is relatively less sensitive to temperature changes. Generally, equilibrium is shifted towards dehydrogenation with rising temperature and decreasing hydrogen concentration.

Satisfactory control of destructive hydrogenation requires that thermal decomposition should produce unsaturated molecular fragments at such a rate that these fragments may be stabilized by hydrogenation before polymerization can take place. The implied mechanism, that stabilization of the products of decomposition occurs through hydrogenation, has been found

satisfactory and coincides with the views of Tropsch (14), Kling and Florentin (10) and Kiss (9). Waterman and Perquin (15), supported by Bruylants' (4) work on coke-oven tars, suggest from a consideration of their results with paraffin wax the view that the primary products of decomposition are stable, and the function of the hydrogen is the prevention of dehydrogenation to unstable bodies capable of polymerization. The appreciable absorption of hydrogen, either gaseous or from the medium, observed in this work makes it probable that Waterman's mechanism plays a minor part in the process.

Assuming the first mechanism, ideal conditions of operation would require a low temperature, a high concentration of reacting substances and catalysts capable of promoting both reactions. At the temperatures used, the rate of hydrogenation of unsaturated molecular fragments must be very great; thus a catalyst capable of promoting hydrogenation is unnecessary. On the other hand, the provision of a high concentration of reactants and the use of a catalyst to ensure adequate supplies of decomposition products at comparatively low temperatures are essential. In this regard, Tropsch (14) and Kling and Florentin (10) have suggested that the primary function of the catalyst is the promotion of the thermal decomposition reaction. The suspension medium offers an excellent means of fulfilment of these conditions by acting as a solvent for the raw material, the thermal decomposition products and hydrogen. A large number of substances may be suggested, but an ideal substance would also act as a hydrogen carrier by maintaining a supply of combined hydrogen greatly in excess of that possible in true solution. Such ideal substances should be capable themselves of rapid reversible hydrogenations. Tetralin (1,2,3,4-tetrahydronaphthalene) is typical of such substances and fulfils the requirements to a large degree.

Tetralin is readily prepared from naphthalene by hydrogenation (13) even on a commercial scale. Hall (6) and others (7, 11) have examined the reaction between hydrogen, naphthalene and tetralin at temperatures as high as 500° C., or higher, and have found that a catalyst is essential. Tetralin is the principal constituent of the equilibrium mixture at 400° C., while decalin appears in small quantities at higher temperatures. Both tetralin and decalin are fairly stable at 400° C., while naphthalene is stable at higher temperatures. Cracking of tetralin to benzene and related compounds is slight at 400° C. and extensive at 450° C. and independent of the presence of a catalyst, excepting the cracking type such as aluminium chloride. It may, therefore, be concluded that tetralin, naphthalene and hydrogen will participate in a rapid reversible reaction at temperatures of about 400° C. in the presence of hydrogen at high pressures and a catalyst like molybdic oxide. The hydrogen atoms in the 1, 2, 3, 4 positions in tetralin are in a highly active state and represent a concentration of two gram molecules of available hydrogen per gram molecule of medium.

The superior action of tetralin as a suspension medium and its ability to hydrogenate coal in the absence of free hydrogen have been reported (2, 3), and are clearly consequences of its unique properties as described. Undoubt-

edly other compounds of a similar nature and value in destructive hydrogenation exist, as a study of patent literature attests, but it is doubtful whether any fulfil the requirement to a degree comparably with tetralin.

In order to confirm the value of tetralin as a suspension medium and to extend the field of application, investigations have been carried out on a number of materials. In what follows, the use of tetralin in the hydrogenation of McMurray bitumen and pitches resulting from distillation of hydrogenated bitumen and coal will be described. The hydrogenation of bitumen in the presence of a variety of catalysts has been reported (1). The material absorbs hydrogen rapidly with the production of light oils. Distillation of the oil and repeated hydrogenation of the residual oils yielded an asphaltic residue, about 15% of the bitumen, that was highly resistant to destructive hydrogenation. In general the heavy oils and pitches resulting from the distillation of hydrogenated bitumen showed great thermal stability and resistance to hydrogenation. The thermal stability, at atmospheric pressure, of the pitches obtained from hydrogenated coal has been remarked upon (2).

Experimental data on the hydrogenation of stable coal tars have been presented by King and Mathews (8) and by Morgan and Veryard (12). According to Morgan the hydrogenation of otherwise resistant residues may be brought about by the use of molybdic oxide and sulphur as catalytic agents in a very high concentration of hydrogen. The effectiveness of this catalyst was shown by King in the continuous hydrogenation of coal tars and of their residues from previous hydrogenation. The most effective means of obtaining rapid and complete reduction to oils was found to be vapor phase hydrogenation at temperatures as high as 500° C.

Materials, Apparatus and Procedure

Bitumen, supplied through the kindness of Dr. K. A. Clark of the Research Council of Alberta, was prepared from McMurray bituminous sands (5). The bitumen was dehydrated by heating it at 110° C. until evaporation of water ceased; it contained 1.5% mineral matter. Its composition has been given (1).

Oils obtained by hydrogenating bitumen were distilled according to the A.S.T.M. gasoline test; the end point of the distillation was 300° C. The pitch-like residues obtained in a number of experiments were combined and this composite pitch was used in the work to be described. The pitch was soft at room temperature and could be distilled to 400° C. at atmospheric pressure without decomposition.

Two types of pitches were obtained from hydrogenated coal exactly as described above (by distillation to 300° C.). One type of pitch was made up of all the residues obtained in experiments in which tetralin was used as suspension medium for coal. This pitch was solid at room temperature and extraordinarily stable to heat. The other type of pitch was made up of residues from experiments in which liquid petrolatum was used as medium (3). This pitch was soft at room temperature and slightly less stable to heat.

The tetralin was Eastman's Practical Grade, b.p. 202–204° C.

The catalyst used throughout was molybdic oxide, prepared by roasting ammonium molybdate and grinding it to pass a 100 mesh screen.

Commercial electrolytic hydrogen as supplied in steel cylinders was used. The apparatus, including the 1800 cc. rocking autoclave with accessories, has been described (1) in detail.

The procedure was identical with that employed in the hydrogenation of coal (3). Weighed amounts of material and medium were thoroughly mixed with the required amount of catalyst and introduced into the autoclave. Hydrogen was admitted until the pressure was that at which it was desired to operate, and the temperature of the autoclave was raised to the operating temperature, which was maintained constant for four hours. The autoclave was then cooled, the gases were withdrawn and fresh hydrogen was admitted. The autoclave was heated for a second period of four hours, and cooled. The gases were then withdrawn, and the autoclave was opened. The liquid and solid products were weighed, separated, and the liquids distilled. The gases were stripped in charcoal absorbers and analyzed.

Results and Discussion

The results of experiments with bitumen and pitch are shown in Tables I and II. The values for hydrogen absorbed, gas produced and the yields of oil, coke and gas are given by weight and based on bitumen or pitch, as the case may be, correction being made for added catalyst and tetralin. The distillation data constitute an exception in being based on the total oil recovered. In these calculations it was assumed that tetralin did not absorb hydrogen or suffer any decomposition or loss. All losses have been assigned arbitrarily to that part of the initial charge consisting of bitumen or pitch. This procedure gives somewhat less favorable results than may be true regarding the production of oil.

Bitumen

The results obtained in Experiments 178 and 179 show that there is little advantage in the use of tetralin. Hydrogen absorption is higher, but coke and gas formation are also higher and the oil yield is lower with tetralin. The lower oil yield may be accounted for in the high loss recorded in Experiment 179.

The oil obtained in Experiment 179 appears to be of a better quality, but the difference in properties may be explained by the presence of tetralin. The yields of pitch, when calculated to a bitumen basis, are almost identical in the two experiments. Evidence of more complete reaction in the presence of tetralin is given by the formation of hydrogen sulphide. Without tetralin, about 33.5% of the sulphur content of the bitumen was removed as hydrogen sulphide. With tetralin, 51% of the sulphur appeared as hydrogen sulphide.

Examination of the pressure-temperature-time records of the experiment shows definitely that better results are obtained when tetralin is used. Fig. 1 gives the pressure-time record for Experiments 178 and 179. The rate of

reaction with tetralin is very much greater, about twice that with bitumen alone, although the pressure drop is much the same in both cases. The action of tetralin may be likened to that of a catalyst in increasing the velocity, without altering substantially the extent, of reaction.

In Experiment 180, tetralin was used as a hydrogenating agent in the absence of hydrogen. Natural gas, 93% methane with traces of ethane and propane and 5% nitrogen, was used in place of hydrogen to create the required high pressure. A considerable quantity of gas, including a small amount of hydrogen, was produced in the reaction and a considerable amount
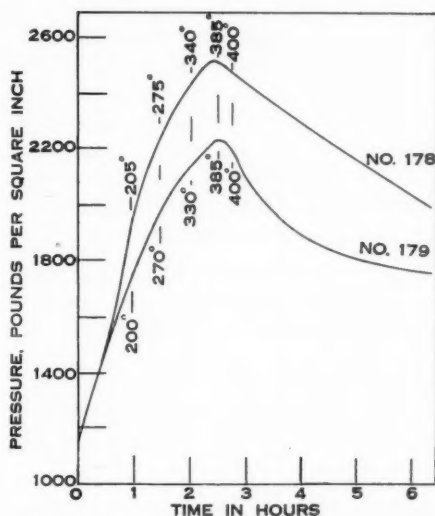
FIG. 1. *Pressure-time relations showing temperatures for the first cycles in the hydrogenation of bitumen with and without tetralin.*

TABLE I

HYDROGENATION OF McMURRAY BITUMEN IN THE PRESENCE OF TETRALIN AT 400° C.

Gas	Hydrogen		Natural gas
Experiment No.	178	179	180
Bitumen, gm.	391	294	302
Tetralin, gm.	0	110	104
Average pressure, lb. per sq. in.			
Initial, cold	1115	1060	1035
Maximum, hot	2575	2450	3510
Final, cold	770	795	1105
Pressure change	−345	−265	70
Hydrogen absorbed, % of bitumen	2.0	2.3	—
Gas produced, l. per kg. bitumen	57.7	82.1	185
Gas—Hydrogen, %	81.6	80.2	3.4
—Hydrogen sulphide, %	3.1	3.6	1.0
Yields, basis bitumen			
Oil, %	85.0	78.0	36.8
Solid, %	6.0	6.7	22.2
Charcoal absorber, %	2.1	2.7	6.3
Gas, %	4.2	4.8	20.4
Loss, %	2.7	7.8	14.3
Oil analysis			
Density	.9236	.9341	.9603
Viscosity, 25° C., poises	.445	.134	.027
Soluble in H_2SO_4, %	50	64	54
Carbon residue, %	6.18	2.83	4.9
Distillation of total oil			
Over at 175° C., %	10.5	9.1	6.3
Over at 225° C., %	16.5	41.3	43.7
Over at 300° C., %	33.0	52.0	57.8
Pitch, %	67.0	48.0	42.2

NOTE:—*Two treatments of four hours each. Catalyst, 5% MoO_3 (by weight).*

of cracking was evident from the high coke yield and fluid nature of the oil. Most of the hydrogen was produced during the first treatment.   On distillation the oil showed a naphthalene content of 33.6%, recovered as crystals.   This amounts roughly to 50% of the tetralin used.   Gaseous hydrogen recovered amounted to 0.675 gm., which corresponds to 22.3 gm. of tetralin.   Evidently more than half of the hydrogen content of the reduced tetralin reacted with the oils.   Assigning all this hydrogen to the bitumen, the absorption was 0.3%.   Undoubtedly the tetralin yielded hydrogen to the bitumen and probably to a greater extent than 0.3%.

In conclusion, it may be said that tetralin acts as a catalyst in the destructive hydrogenation of bitumen.   Its presence is beneficial from the point of view of increasing the rate of reaction rather than of increasing the conversion to oils.

Pitches

The results of experiments on the hydrogenation of pitches recovered from hydrogenated bitumen and coal are given in Table II.

It was shown previously (1) that the pitch obtained from hydrogenated bitumen possessed great stability, and could be decomposed and hydrogenated only in the presence of aluminium chloride at 460 to 500° C.   Experiments 176 and 177 were comparative experiments on such a pitch, with and without the addition of tetralin.   There was a noticeable gain in oil yield and decrease in coke and gas yield in the presence of tetralin.   The pressure-time and pressure-temperature charts failed to show any difference in the rate of reaction.   The benefits apparent in Experiment 177 are not all real, however, since the yield of pitch, based on bitumen, is greater.   It may be concluded that the use of tetralin is of no great benefit.

The hydrogenation of pitches recovered from hydrogenated coal was also carried out with and without tetralin.   The results (Experiments 172 to 175) are shown in Table II.   The temperature, 450° C., employed in these experiments was the only condition that differed from the conditions existing in the experiments discussed above.   This difference is significant, however, since Hall (6) has shown that the decomposition of tetralin under such conditions is appreciable.

Contrary to expectations, tetralin had no great effect on the hydrogenation of the less stable pitch obtained from coal and petrolatum.   A higher hydrogen absorption and production of a better quality oil in the presence of tetralin suggested that the reaction was not the same in each case, but no difference in rate of reaction was discernible in the pressure-time-temperature records.

With regard to Experiments 173 and 174, in which pitch obtained from hydrogenated coal and tetralin mixtures was treated, the results offer some evidence of a beneficial action due to tetralin.   The yield of oil, based on bitumen alone after subtracting the added tetralin, was more than 71% in Experiment 173, compared with 67% in Experiment 174.   Hydrogen absorption was greater and coke formation less on the same basis in the presence of

TABLE II

HYDROGENATION OF PITCHES IN THE PRESENCE OF TETRALIN

Pitch type	From bitumen		From coal and petrolatum		From coal and tetralin	
Experiment No.	176	177	172	175	174	173
Pitch, gm.	399	293	390	356	387	268
Tetralin, gm.	0.0	98	0.0	42	0.0	129
Temperature, °C.	420	420	450	450	450	450
Average pressures, lb. per sq. in.						
Initial, cold	1100	1060	930	1135	1065	1035
Maximum, hot	2360	2500	2245	2740	2495	2360
Final, cold	640	750	670	820	555	610
Pressure change	−460	−310	−260	−315	−510	−425
H_2 absorbed, % of pitch	2.4	2.3	1.6	2.3	2.8	3.4
Gas produced, l. per kg. pitch	75.6	61.3	48.6	95.0	90.6	156.0
H_2 in gas, %	71.7	82.3	83.0	72.8	62.2	71.8
Yields, basis pitch						
Oil, %	84.3	94.2	89.5	87.0	67.2	71.7
Solid, %	5.8	3.5	0.0	0.9	13.9	5.3
Charcoal absorber, %	2.7	2.4	1.3	3.9	2.1	4.5
Gas, %	6.8	3.9	3.3	9.6	9.3	11.3
Loss, %	0.4	Gain	5.9	Gain	7.5	7.2
Distillation of total oil						
Over at 175° C., %	3.1	2.3	4.7	13.5	1.6	6.6
Over at 225° C., %	6.6	22.4	8.0	28.2	8.6	30.7
Over at 300° C., %	17.2	36.7	21.1	50.0	22.5	43.1
Pitch, %	80.5	63.2	78.9	49.6	76.7	52.9
Loss, %	2.3	0.1	0.0	0.4	0.8	5.0

NOTE:—*Two treatments of four hours each.   Catalyst, 5% MoO₃ (by weight).*

tetralin.   On the other hand, no difference in rate of reaction was found in the two experiments.   It may be suggested that the difference between the results of these pairs of experiments is due to the different composition of the two pitches.   The pitch used in Experiments 172 and 175 would be richer in saturated hydrocarbons, and that used in Experiments 173 and 174 would be richer in polynuclear compounds.

From the point of view of continuous operation in the reduction of bitumen and of coal to oils, the conversion of the resistant pitches is of importance. The foregoing results do not offer much hope that such conversion can be accomplished.   However, the results are not extensive enough to make a final conclusion possible.   Further experiments, in which higher temperatures or cracking catalysts such as aluminium chloride are used, should be carried out in order to determine under what conditions these pitches may be reduced.

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HYDROGENATIONS IN A TETRALIN MEDIUM

II. DESTRUCTIVE HYDROGENATION OF COAL WITH TETRALIN AND WITH A MIXTURE OF RELATED COMPOUNDS AS MEDIA[1]

By E. H. Boomer[2] and J. Edwards[3]

Abstract

A complex mixture of polynuclear hydrocarbons obtained in the pyrolysis of natural gas has been hydrogenated. The original mixture and the product of hydrogenation have been used as suspension media in the hydrogenation of bituminous and domestic coals, and are compared with tetralin as a medium. The original mixture is much less, and the hydrogenated mixture only slightly less, effective than tetralin.

Introduction

In the first of this series of papers (2), the use of tetralin as a medium in destructive hydrogenation processes was discussed, and it was suggested that other substances might serve with similar results. The present paper gives results of experiments in the hydrogenation of coal in which a fluid mixture of aromatic hydrocarbons known as pyrolysis tar was used as suspension medium.

A large body of literature exists on the hydrogenation of aromatic hydrocarbons, including polynuclear compounds such as naphthalene, anthracene and others (8). Hydrogenation proceeds smoothly and rapidly under proper conditions of moderate temperatures and pressures of hydrogen in the presence of a catalyst. Decomposition reactions begin as the temperature approaches some limiting value, usually near 400° C. (9), and the final product contains paraffins, cycloparaffins and hydro-derivatives of polynuclear hydrocarbons. The use of polynuclear hydrocarbons and their hydro-derivatives in destructive hydrogenations has been mentioned frequently in the patent literature (6), but relatively little has been published in detail. The use of naphthalene and tetralin as media in the hydrogenation of Alberta coal has been reported (4, 5). Beuschlein *et al.* (1), in a series of reports, described the use of anthracene and diphenyl as media in the hydrogenation of American coals. He obtained higher percentage conversions with anthracene.

Materials and Apparatus

Two low-rank Alberta coals, Nos. E-305 and J-309, classified in the Canadian system as bituminous and domestic respectively, were used. Analyses of these coals and the method of preparing them for use, which consisted of drying and grinding them in an inert atmosphere, have been given (5). The coals contained 10.1% and 8.8% ash, on a dry basis.

The pyrolysis tar was obtained as a product of the pyrolysis of natural gas at 950° C. (7). This material was a black, fluid, highly complex mixture of aromatic hydrocarbons. Distillation analysis of the material in an A.S.T.M. gasoline apparatus gave the results shown in Table I. Of the large number of hydrocarbons in the material, benzene, toluene, styrene, chrysogen, chrysene and diphenyl methane occur in small amounts and have been identified. Naphthalene and anthracene were present in large amounts, the former constituting about 25%, and the latter 5%, of the mixture.

TABLE I

A.S.T.M. DISTILLATION OF PYROLYSIS TAR

10% over at 208	50% over at 309
20% over at 225	60% over at 325
30% over at 244	70% over at 386
40% over at 269	73.5% over at 390

NOTE:—*Initial b.p. 90° C.; barometric reading, 670 mm. of mercury.*

Finely divided solid material, high in carbon and insoluble in all common solvents, was present as a stable suspension to the extent of 9% by weight. On removal of this material the tar became dark brown.

Molybdic oxide, prepared by roasting ammonium molybdate, was employed as a catalyst in all experiments. Commercial electrolytic hydrogen was used as supplied.

The apparatus, an 1800 cc. oscillating autoclave, and the procedure, have been described in detail (3).

Results and Discussion

All percentage data are given on a weight basis and refer either to the total of coal and ash, on a moisture free basis, plus medium, or to the coal and ash, on a moisture free basis, alone. While the solid residue obtained in these experiments was generally more than half inorganic material, consisting of ash and catalyst, the data tabled refer only to the organic portion. In Experiment 186 the data refer of course to pyrolysis tar only. Under the heading "conversion of coal, A M F basis", all losses and gas production have been assigned to the coal and none to the medium. The original weight of medium was subtracted from the total oil yield to give the yield of oil from coal. The procedure is arbitrary and does not give a correct presentation of the conversion of coal to oil. Most of the losses occurred in connection with the liquid products and should be assigned to both coal and medium. A division of the losses is, however, impossible. Gas was also produced through decomposition of the medium, an idea of the amount being given by the results of Experiment 186, but again a division cannot be made. The most accurate data on the conversion of coal for comparative purposes are shown under "per cent solids".

Treatment of the tar alone, Experiment 186, resulted in rapid absorption of hydrogen. The high yield of solid, 9%, does not represent the true coke formation, as about 9% of free carbon was present initially in the pyrolysis

TABLE II

HYDROGENATION OF PYROLYSIS TAR, AND ITS USE AS A SUSPENSION MEDIUM IN THE HYDROGENATION OF COAL

Experiment No.	186	183	188	189	187	155	161
Medium	Pyrolysis tar			Hydrogenated pyrolysis tar		Tetralin	
Coal sample no.		E-305	J-309	E-305	J-309	E-305	J-309
Medium, gm.	505	204	182	190	199	150	150
Coal, gm.	—	191	182	195	199	200	200
Temperature, °C.	425	450	450	450	450	450	450
Average pressures, lb. per sq. in.:—							
Initial, cold	1120	1090	1115	1120	1130	1000	1045
Maximum, hot	2425	2720	3080	2740	3340	2570	2950
Final, cold	480	435	500	505	500	510	585
Pressure change	−640	−655	−615	−615	−630	−490	−460
Hydrogen absorbed, % AMF coal	2.2	4.1	4.2	3.8	3.7	3.4	3.4
Gas produced, l. per kg. AMF coal	47.0	118	102	115	123	85.0	94.3
Hydrogen in off-gas, % by volume	70.0	44.3	53.9	54.3	48.2	72.0	71.5
Yields, basis AMF coal plus medium							
Liquids, %	85.9	61.2	71.5	77.9	69.0	75.7	72.0
Solids, %	9.0	19.9	10.3	6.3	8.2	7.1	1.8
Charcoal absorber, %	0.8	3.2	2.8	2.8	3.2	4.1	4.2
Gases, %	3.3	10.3	10.5	10.8	12.5	8.7	13.7
Losses, %	1.0	5.4	4.9	2.2	7.1	4.4	7.7
Conversion of coal, AMF basis							
Solids, %		43.4	21.2	13.4	17.5	13.0	3.3
Oils, %		13.8	32.1	49.5	22.8	52.6	41.5
Water, %		1.4	8.6	4.2	11.9	2.8	8.5
Charcoal absorber, %		7.0	5.9	5.8	6.7	7.5	7.7
Gases, %		22.6	22.0	22.5	26.2	16.0	25.0
Losses, %		11.8	10.2	4.6	14.9	8.1	14.0
Distillation of total liquids							
Over at 175° C., %	2.0	4.5	9.6	8.4	11.2	5.3	10.2
Over at 225° C., %	27.3	29.2	32.2	32.9	33.5	55.5	59.8
Over at 300° C., %	50.5	49.8	49.3	49.0	53.0	67.0	71.3
Pitch, %	48.4	49.1	45.0	48.4	37.8	30.6	22.3
Water, %	0.0	1.1	5.7	2.6	8.3	2.0	6.4
Loss, %	1.1	0.0	0.0	0.0	1.0	0.4	0.0

NOTE:—*Two treatments of four hours each.   Catalyst, 5% MoO$_3$.*

tar. It may be concluded that coke formation was really negligible. The distillation curve of the oil recovered was similar to that of the original tar. The oil was, however, much less viscous than the tar and of more pleasant odor. On distillation, about 14% of the oil came over between 200 and 205° C. at a pressure of 700 mm. of mercury. This fraction would be largely tetralin. No naphthalene crystallized from the fractions 210–215° C. and 215–220° C. This oil, containing probably, paraffins, cycloparaffins and hydro-derivatives of polynuclear hydrocarbons, was used directly as medium in Experiments 187 and 189 on coal.

The pressure-time curves, for both treatments, with temperatures taken every half hour, are shown in Fig. 1. Even after four hours the pressure was still falling slowly during the second treatment, indicating that hydrogenation was still incomplete. As is generally true, the maximum pressure was less and the rate of pressure drop was greater in the first treatment than in the second.

FIG. 1. *Experiment 186. Pressure-time relations with temperatures for both cycles in the hydrogenation of pyrolysis tar.*

In Experiment 183, pyrolysis tar was used as medium with bituminous coal, and a fair conversion obtained. The conversion of coal to liquids and gases, plus the losses, 56.6%, while much less than that found with hydrogenated tar or tetralin, is comparable with the conversion of 54.2% obtained with a liquid petrolatum medium (5). It is believed that the low conversion is due to the inability of bituminous coal to compete with pyrolysis tar for a limited supply of hydrogen. The use of hydrogenated tar as medium, as tabled under Experiment 189, gave results directly comparable to those obtained with tetralin in Experiment 155. It should be pointed out, however, that the ratio of hydrogenated tar to coal was 1.0, while that of tetralin to coal was only 0.75. In addition, a better and lighter oil was obtained in Experiment 155. The higher gas yield, higher hydrogen absorption and lower hydrogen content of the off-gas in the presence of tar or hydrogenated tar may be attributed to deficiencies of the media as compared with tetralin.
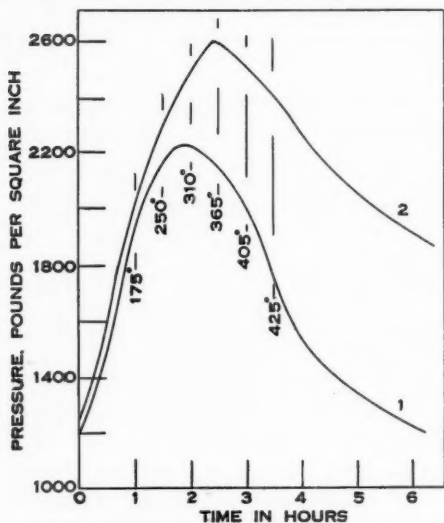

FIG. 2. *Experiments 183 and 189. Pressure-time relations for the first cycles in the hydrogenation of coal in pyrolysis tar. Bituminous coal.*

The pressure-time-temperature data for the first treatments in Experiments 183 and 189 are shown in Fig. 2. The unsaturated nature of the pyrolysis tar is reflected in the lower temperature at which reaction begins and the greater rate of pressure drop in Experiment 183. Except for a more rapid pressure drop, the curve for Experiment 189 is similar to the corresponding curve for Experiment 155. The initial reaction temperature and reaction rate are related to the degree of unsaturation of the suspension medium.

The behavior of domestic coal, No. J-309, in Experiments 187 and 188 indicates again that pyrolysis tar, particularly when hydrogenated, is a satisfactory suspension medium. In general, the relations among the three media in Experiments 161, 187 and 188 are much the same as for Experiments 155, 183 and 189, when account is taken of the difference between the coals. Domestic coal is more easily hydrogenated than bituminous coals, although the oil yield may be smaller because of the large amount of water and gas formed. The high conversion of coal to liquids and gases obtained with pyrolysis tar, plus losses, of 78.8%, may be compared with 68.1% obtained with liquid petrolatum (5). This high figure would suggest that domestic coal can compete with pyrolysis tar for hydrogen rather more successfully than can bituminous coal. Hydrogenated tar is definitely better as a medium although not as effective as tetralin. However, it is believed that pyrolysis tar can be hydrogenated so as to produce a product substantially as effective as tetralin.

Fig. 3 presents the pressure-time-temperature data of the first treatments of Experiments 187 and 188. The low temperature at which reaction began and the low maximum pressure in Experiment 188 show the unsaturated nature of the medium. The relatively short time required for the pressure to become constant may be attributed to the reactivity of domestic coal.

In conclusion, it may be said that pyrolysis tar can be hydrogenated readily, and the resulting oil shows promise as an effective suspension medium in the reduction of coal to oils. The good results obtained with a medium of hydrogenated tar are due to the presence of tetralin and other hydro-derivatives of polynuclear hydrocarbons. The results are of some practical value in connection with the utilization of waste natural gas.
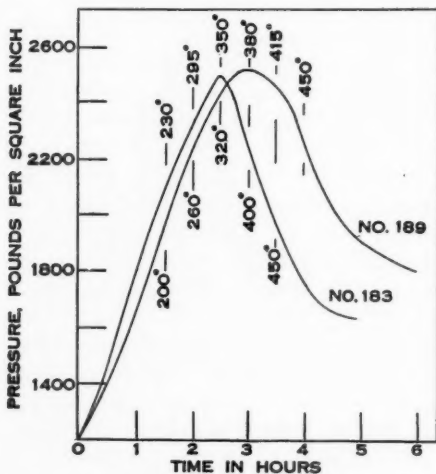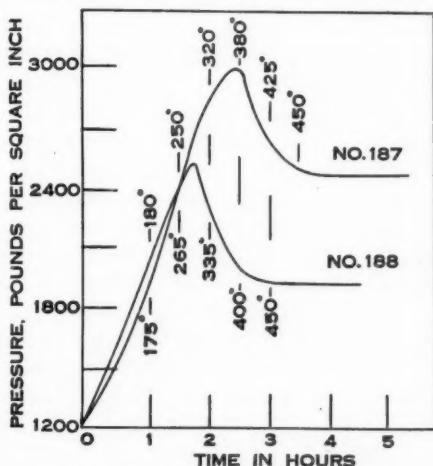

FIG. 3. *Experiments 187 and 188. Pressure-time relations for the first cycles in the hydrogenation of coal in pyrolysis tar. Domestic coal.*

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HYDROGENATIONS IN A TETRALIN MEDIUM

III. DESTRUCTIVE HYDROGENATION OF CELLULOSE AND WOOD[1]

BY E. H. BOOMER[2], G. H. ARGUE[3] AND J. EDWARDS[4]

Abstract

The destructive hydrogenation of cotton wool cellulose and fir wood sawdust in a tetralin medium was investigated. When it is present in sufficient excess, tetralin promotes the complete conversion of cellulose and wood to liquids and gases in the absence of a catalyst. The tetralin acts as a hydrogen carrier in fulfilling the function of a catalyst.

Introduction

Continuing this series on the value of tetralin as a suspension medium in destructive hydrogenations (2), the present paper presents the results of some experiments with cotton wool cellulose and fir wood sawdust.

The hydrogenation of cellulose and wood has attracted the attention of many investigators. Palmer (11, 12), in a study of the distillation of birch wood in which phosphoric acid was used as catalyst, observed increased yields of methanol at moderate pressures (60 to 150 lb. per sq. in.). Hawley (9) failed to confirm the finding with regard to the value of phosphoric acid, but found improved yields with lime, calcium and sodium carbonate. Bergius (1) subjected cellulose to thermal decomposition in a closed vessel under the pressure of the autogenous gases. The coal-like substance obtained was hydrogenated and a small quantity of oil resembling petroleum was formed. Bowen, Shatwell and Nash (5) found that at 420–440° C. there was no appreciable production of liquid from cotton cellulose in the presence of hydrogen at 40 atm. Nickel catalyzed the production of oils, however, but iron and vanadium did not. Bowen and Nash (4) found a nickel and alumina catalyst particularly effective, and that more than 80% of the cellulose was converted to liquids and gases. Methane was present in the gases. Fierz-David and Hannig (6), in their investigations on cellulose and wood, found that distillation was not affected by the presence of hydrogen at a pressure of 300 atm. unless a catalyst, nickel, were present. Copper was less effective, and iron, of little effect. In the presence of nickel, the conversion to gases and liquids was almost quantitative, the liquids containing alcohols, aldehydes, ketones, acids, furans and phenols in addition to water. In general, it has been found that carbon dioxide is the chief gaseous product at low decomposition temperatures, carbon monoxide, hydrogen and methane appearing at higher tem-

peratures. Waterman and Perquin (13) have confirmed the observations that cellulose is not hydrogenated to oils in the absence of a catalyst, although a 38% yield of a viscous yellow oil was obtained by vacuum distillation of cellulose. The use of a suspension medium of Borneo petroleum resulted in less coke and more hydrocarbons being formed. Frolich *et al.* (7) reported on the treatment of sulphite pulp cellulose and wood under pressure of hydrogen, nitrogen and autogenous gases. More than 90% of the wood was converted to liquids and gases in the presence of nickel. Cellulose was almost completely converted by hydrogenation in the presence of nickel, but the use of nitrogen with nickel resulted in the production of 14% of coke. Lindblad, using a variety of catalysts in an extensive investigation on the hydrogenation of wood (10), found that nickel and cobalt were effective in promoting conversion of wood to tar at 250° C. Methane was formed at higher temperatures. Hydrogenation of sawdust impregnated with cobalt sulphide at 350° C. resulted in a 40% yield of oils, and a large hydrogen absorption (approximately 5%). The use of sulphite liquor as suspension medium and ferrous sulphide as catalyst yielded excellent results, *e.g.*, conversions of 58% to oils and 12.4% to water, a residue of 13%, and a hydrogen absorption of 5.5% by weight of the wood.

The present paper describes experiments in which tetralin was used as suspension medium without any catalyst other than the walls of the reactor, and which showed high conversions of cellulose and wood to liquids and gases. The work is of a preliminary nature and demonstrates chiefly the effectiveness of tetralin as a medium.

Materials and Apparatus

The cellulose used was a commercial grade of absorbent cotton. British Columbia fir wood sawdust containing 0.31% ash and 5.2% moisture was dried at 110° C. and used without further treatment. Tetralin of a practical grade, b.p. 204–206° C., and commercial electrolytic hydrogen were employed.

Two types of apparatus have been used. The results in Table I were obtained on small amounts of materials in a small vertical autoclave of 180 cc. capacity and fitted with a glass thimble as liner. The materials were introduced into the autoclave in the glass thimble, closure was effected, the apparatus flushed with hydrogen and the hydrogen pressure raised to 1000 lb. per sq. in. The autoclave and attached recording pressure gauge were isolated from the rest of the apparatus by means of valves, and the temperature was raised to the desired operating value as rapidly as possible. The temperature was kept constant by means of an automatic controller governed by a thermocouple. After a chosen reaction time, the autoclave was cooled to room temperature, the gases were drawn off and analyzed, and the autoclave was opened for removal of liquid and solid products.

The experiments listed in Table II were carried out with larger samples of wood in an 1800 cc. oscillating autoclave already described (3).

Results and Discussion

The results shown in Table I were obtained with the use of relatively large amounts of tetralin as compared to those of cellulose and wood. Certain characteristics were common to all these experiments. The pressure rose with the temperature to a maximum value, as tabled, and remained constant thereafter while the temperature was constant. The water recovered was in all cases strongly acid, and the odor of the light oil was similar to that of aldehydes. The initial boiling point of the liquid was always lower than 50° C. The solid residues adhered very firmly to the glass container and could not be weighed with any degree of accuracy. In Table I, "Trace",

TABLE I

HYDROGENATION OF CELLULOSE AND WOOD IN TETRALIN AT 350° C.

	Cellulose			Wood		
Experiment no.	5	7	8	9	10	11
Material, gm.	8	8	12	18.6	15.2	15.2
Tetralin, gm.	48.6	58.3	0	58.3	58.3	0
Gas, 1000 lb. per sq. in.	H_2	CH_4	H_2	H_2	CH_4	H_2
Maximum pressure, hot, lb. per sq. in.	2800	4150	3600	3850	4050	2275
Solid residue, gm.	Trace	Small	Large	Trace	2.5	7.8
Liquid recovered, cc.	50	60	1.0	69	65	0.3
Distillation of liquid						
Water, cc.	1.5	2.0	Trace	4.1	2.7	Trace
Oil to 200° C., cc.	2.5	1.5	Trace	2.5	1.5	Trace
Pitch, cc.	5.0	3.2	Trace	12.4	5.0	Trace
Naphthalene, cc.	—	2.0	—	—	2.0	—
Gas analysis, not including added gas						
CO_2, %	47.6	32.0	59.4	51.4	48.1	48.4
CO, %	18.7	22.2	13.0	12.2	32.3	11.5
Olefines, %	1.5	2.6	0.0	1.1	5.3	1.6
CH_4, %	24.2	—	14.5	28.6	—	38.5
C_2H_6, %	7.8	—	13.0	6.6	—	0.0
H_2, %	—	43.0	—	—	14.3	—
Hydrogen in off-gas, %	87.6	6.6	85.8	53.0	1.9	74.9
Hydrocarbons in off-gas, %	—	78.9	—	—	84.8	—

as applied to the solid residue, means that it consisted of a black film of a tarry nature on the glass surface. By "Small" is meant this same black film with a few grains of imbedded coke. "Large" indicates that the solid residue appeared to be unchanged starting material, except that the color was black.

Preliminary experiments were carried out with cellulose at 200, 250 and 300° C. At 200° C. reaction was very slight and no liquid products were formed. The cellulose was apparently changed only in color. Carbon dioxide, carbon monoxide and methane appeared in small amounts in the off-gas. At 250° C. reaction was more evident, but the solid residue was still large, of the same form as the original cellulose, and was black and slightly charred. Distillation of the liquid through a micro-column yielded traces

of acidic water, light oil and 3 gm. of a high boiling tar.   At 300° C. dissolution of the cellulose was almost complete, leaving only a small residue.   On distillation of the liquid, 0.5 gm. of light oil, 0.2 gm. of water and 2.5 gm. of tar were recovered from a 40 cc. sample of the liquid in the autoclave.

Experiments 5, 7 and 8 were comparative experiments carried out to demonstrate that tetralin was largely responsible for dissolution of the cellulose. In Experiment 5, with hydrogen and tetralin, the cellulose disappeared completely, leaving only a black tar film on the glass.   In Experiment 7 the hydrogen was replaced by natural gas, largely methane.   While the cellulose was not completely dissolved, the residue was very small and not recoverable. The identification of naphthalene in the liquid recovered showed that some dehydrogenation of tetralin had taken place.   In Experiment 8 it was demonstrated that tetralin is essential to the reduction of cellulose.   In this experiment the cellulose was charred but retained its original physical form. The liquid residue appeared to be largely water.

The gas analyses are interesting in showing that methane and ethane together form the major portion of the gas.   The analyses are based on the off-gas less the original gas (hydrogen in the case of Experiments 5 and 8 and natural gas in Experiment 7).   Experiment 7 shows that hydrogen is a product of the reaction, although it is unknown to what extent tetralin is the source. Hall (8) states that tetralin becomes unstable at temperatures higher than 400° C., but he did not find naphthalene to be completely converted to tetralin at 350° C.

Experiments 9, 10 and 11 on wood constituted a series corresponding to that on cellulose, and demonstrate conclusively that tetralin is required for the dissolution of wood.   Except for the change in color to black, the sample of wood used in Experiment 11 was apparently unaltered.   A trace of liquid was formed and carbon dioxide, carbon monoxide and methane were produced, showing that some reaction occurred.   As with cellulose, tetralin alone was able to reduce wood to liquids and gases rather effectively, naphthalene being produced in the process.

It is evident that tetralin is an efficient medium in which to carry out the hydrogenation of cellulose and wood.   In view of the fact that a catalyst is necessary, as demonstrated in previous investigations already discussed, and the results found in the present work in which no catalyst was used, it appears that tetralin also fulfils the function of a catalyst.

In Table II are shown the results of three experiments with dry fir sawdust on a larger scale than those reported in Table I.   Apart from the larger scale, the essential difference between these experiments and those listed in Table I lies in the tetralin-wood ratio.   Here the ratio is 1 or 1.2 to 1, compared to about 3 or 4 to 1 in Experiments 9 and 10.

The material removed from the autoclave contained much volatile material, and losses occurred before the weight could be determined.   After it was weighed, the material was filtered, and the solid residue washed with ether,

dried and weighed.   It was considered that this solid material, coke-like in appearance, was formed solely from the wood.   The losses were due largely to evaporation of the volatile products of the reactions and only in small part to losses of solvent.   For this reason the conversion figures in Table II show

TABLE II

HYDROGENATION OF WOOD IN TETRALIN

Experiment no.	16	17	18
Tetralin, gm.	180	198	148
Wood, gm.	152	163	149
Temperature, °C.	325	350	325–375
Pressures, lb. per sq. in.			
Initial, cold	1200	1220	1140
Maximum, hot	3435	3740	3475
Final, cold	1175	1205	1140
Hydrogen absorbed, % weight of wood	2.5	3.3	3.7
Gas produced, less H_2, litres	5.3	6.8	10.9
Yields, basis charge,			
Solids, %	34.3	20.2	23.9
Liquids, %	56.9	68.7	65.0
Gases, %	1.1	1.2	1.3
Loss, %	7.7	9.9	9.8
Conversion of wood,			
Solids, %	75.0	44.8	47.7
Oil, gas, and loss, %	16.5	46.0	42.2
Water, %	8.5	9.2	10.1
Distillation of liquid			
Water, %	6.9	8.7	7.8
Oil to 175° C., %	1.7	2.3	1.7
Oil to 225° C., less 200–206° C.			
fraction, %	5.8	12.7	13.1
Oil, 200-206° C., %	80.4	68.4	64.3
Pitch, above 225° C.	6.9	10.2	14.8
Gas analysis			
CO_2, %	7.0	8.0	4.3
Olefines, %	0.0	0.4	0.0
H_2, %	89.2	81.3	90.6
CO, %	0.9	1.3	0.6
CH_4, %	2.9	7.3	3.3

all the losses combined with the figures for oil and gas.   The oil was distilled until the temperature was 50° C. and the distillate, largely ether, was discarded.   No doubt some volatile products of the reaction were contained in this ether fraction.   The remaining oil was fractionated in a 14-in. packed column, and the results are tabled.   Assuming the fraction 200-206° C. to be mostly tetralin, the recovery of tetralin is quite high, more than 80% in Experiments 16 and 18 and more than 90% in Experiment 17.

Experiments 16 and 17 were single treatments of one and two hours' duration respectively, while Experiment 18 was a double treatment experiment at 325° C. in the first and 375° C. in the second treatment.   The data on conversions are based on the solid residue and water recovered.   The yield of oil and gas is a much less certain quantity, including, as stated above, all the losses consequent to handling the material.

The conversion at 325° C. is small but probably due to hydrogenation more than to thermal decomposition. The absorption of hydrogen is large enough to suggest that reduction of the wood occurred, although some of the hydrogen may have combined with tetralin.

Experiment 17 is directly comparable with Experiment 9, Table I, in that both were carried out at 350° C. The difference in conversion may be attributed to the difference in relative amounts of tetralin. It is suggested that the large excess of tetralin in Experiment 9 permits very rapid hydrogenation of the primary products of thermal decomposition of wood. In the absence of a large excess of tetralin, thermal decomposition may proceed to coke formation because of a slower rate of hydrogenation.

In Experiment 18 the wood was treated first at 325° C., and second, with a fresh supply of hydrogen at 375° C. in an endeavor to increase the conversion. It was apparent that the results were slightly less satisfactory than those obtained at 350° C. with one treatment. There were no great differences in the results of Experiments 17 and 18, although a more extensive reaction is suggested by the higher hydrogen absorption and water production in the latter.

The results of these experiments indicate that wood can be successfully hydrogenated in the presence of tetralin without a catalyst. The temperature should be greater than 325° C. and preferably about 350° C. It is essential for complete reduction to oils and gas that the tetralin be present in relatively large excess, not more than 3 parts of tetralin to 1 of wood, but certainly more than 1.2 to 1.

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HYDROGENATIONS IN A TETRALIN MEDIUM

IV. DESTRUCTIVE HYDROGENATION OF GRAIN SCREENINGS[1]

By E. H. Boomer[2] and J. Edwards[3]

Abstract

The destructive hydrogenation of grain screenings in a tetralin medium has been investigated. With an excess of tetralin, at least 3 to 1 by weight, more than 50% of the screenings can be reduced to oils and about 15% to solid residue. Catalysts are effective by virtue of the fact that they greatly increase the rate of reaction, and also increase the production of hydrocarbon gases at the expense of carbon dioxide.

Introduction

In a previous paper of this series (1), it was shown that tetralin is a most efficient suspension medium in the hydrogenation of cellulose and wood. In view of the general similarity of the properties of grain screenings, cellulose and wood, it was suggested by Dr. W. H. Cook* that an investigation of the process as applied to screenings would be of interest.

Grain screenings consist of a mixture of weed seeds, grain, seed coats and chaff, and accumulate in large amounts at the elevators in Fort William and Port Arthur each year, and their disposal presents a serious problem. The screenings consist largely of cellulose and lignin, but contain in addition ·considerable amounts of vegetable oil by virtue of their seed content. A market exists for part of the material as stock feed, and various suggestions have been made regarding the use of the surplus as fuel or as a source of vegetable oils. The present paper does not pretend to suggest an outlet for grain screenings; it is an account of a preliminary investigation that may be of some possible future interest.

Materials and Apparatus

Grain screenings were supplied as collected and in four different fractions. A description of these appears in Table I together with that of a sixth material, which consisted of equal parts of the solid residues from the hydrogenation of Samples 4 and 5.

Sample 1, whole grain screenings, was made up of equal parts of Samples 2 to 5. Any one sample was not particularly free from the constituents of the other samples, but was predominantly as described.

Tetralin of a practical grade, b.p. 204–206° C., was used throughout, and the hydrogen was the usual electrolytic grade.

TABLE I

MATERIALS

Sample no.	Dry matter as % of wet weight	Description
1	91.4	Whole grain screenings
2	90.8	Black seeds, lamb's-quarter and small seeds, etc.
3	91.4	Refuse screenings, very fine material, seed coats and chaff
4	91.3	Refuse screenings, coarser than No. 3
5	91.5	Ragweed screenings, grain, large material
6	100.0	Solid residues from hydrogenation of Nos. 4 and 5 in equal parts.

Two types of apparatus and procedure were used, the first permitting batch operation, and the second, semi-continuous operation.   They will be described in connection with the results.

Results and Discussion

The data obtained in this work are given in Tables II and III.   Table II presents results obtained in preliminary work, in which a batch method was used with the different samples of screenings.   Table III presents results obtained with dry whole screenings, Sample 1, with a semi-continuous method of operation and larger relative amounts of tetralin.

Batch Hydrogenations

The apparatus and procedure have been described in all their essentials previously (2).   Briefly, the screenings and tetralin were weighed, introduced into an 1800 cc., oscillating autoclave, hydrogen was admitted and the temperature raised to that desired.   After two hours at constant temperature, the autoclave was cooled, the gas drawn off, metered and analyzed, and the autoclave opened.   The material in the autoclave was removed as completely and expeditiously as possible, weighed and filtered.   The residue on the filter was washed with ether until free from oil, dried and weighed.   The ether-oil solution was heated on a water bath, and the ether taken off together with some of the volatile constituents of the oil.

The data given in Table II are all on a weight percentage basis.   In calculating the conversions of screenings to solid, liquid and gas, all the losses were assigned to the screenings.   The original weight of tetralin was subtracted from the weight of liquids recovered.   The high and variable losses were due to difficulties in handling the material and inability to prevent losses by evaporation during the process of emptying the autoclave.   There is no doubt that part of the loss should be assigned to the tetralin.   The yields of gas and solid residue are the most trustworthy data, and the sum of the oil yield and loss will give a better measure of the conversion of screenings to oil than the figures tabled.   The gas production, given in litres at a pressure of 760 mm. of mercury and 0° C., does not represent the true value, inasmuch

as the hydrogen has not been included. It is highly probable that hydrogen is produced in the reaction to some extent. The recovered oil was fractionated in a 14 in. packed column, and the results are tabulated as percentages of the total liquid recovered, including water. These figures do not include the more volatile products lost during the ether treatment. The initial boiling point of the crude oil always lay between 50° and 60° C., while the recovered

TABLE II

BATCH HYDROGENATION OF GRAIN SCREENINGS IN TETRALIN WITHOUT A CATALYST

Sample no.	1	2	3	4	5	6
Screenings, gm.	367	345	267	295	311	245
Tetralin, gm.	236	210	200	211	244	196
Temperature, °C.	350	250–350	325	300	325	350
		(1)–(2)				
Pressures, lb. per sq. in.						
Initial, cold	1110	1170–1100	935	990	1115	1095
Maximum, hot	4920	2960–4350	3420	2560	4040	2390
Final, cold	1235	1170–1100	1035	755	1205	785
Conversion of screenings						
Solids, %	39.5	51.6	55.8	62.0	69.5	73.5
Liquids, %	31.6	21.4	19.9	21.4	8.4	16.3
Gases, %	7.0	4.2	4.7	4.6	5.0	0.7
Losses, %	21.9	22.8	19.6	12.0	17.1	9.5
Gas yield, less hydrogen, litres	35.8	17.9–10.0	18.6	21.9	21.9	3.4
Gas analysis:—						
CO_2, %	26.2	19.1–11.7	21.7	27.6	20.2	4.6
CO, %	1.0	0.5– 0.6	1.2	1.0	0.5	0.5
H_2, %	60.5	76.1–82.6	72.0	64.3	73.9	91.2
CH_4, %	10.5	2.1– 4.7	5.3	4.8	5.2	3.6
C_2H_6, %	1.3	0.0– 0.0	0.0	0.9	0.0	0.0
Distillation of liquid recovered:						
Water, %	9.6	13.7	9.0	3.9	9.9	0.9
Oil, less 200–206° C. fraction:						
Over at 175° C., %	1.9	2.1	0.9	0.4	4.0	1.7
Over at 225° C., %	5.3	6.6	6.3	5.7	10.3	4.7
Over at 300° C., %	8.9	13.3	12.4	10.5	13.9	11.1
200–206° fraction, %	62.7	53.1	63.3	71.6	55.1	76.0
Pitch, %	18.1	19.9	14.9	12.7	21.1	12.0
Loss, %	0.7	0.0	0.4	1.3	0.0	0.0

NOTE:—(1) *First treatment.* (2) *Second treatment.*

oil, as entered in the table, showed initial boiling points between 76° and 80° C. The data on the 200–206° C. fraction have been tabulated separately to indicate roughly the tetralin content of the oil. Assuming this fraction to consist substantially of tetralin, more than 90% of the initial quantity was recovered in experiments on Samples 1, 4 and 6.

Limited amounts of each sample, except No. 1, were available and one experiment only was carried out with each. The use of different conditions for each sample was justified on the assumption that the various fractions would behave nearly alike. Only one constituent, black seeds, showed a definite difference from the others in its resistance to destruction. While all other constituents were destroyed or formed amorphous coke at 300 to 325° C., black seeds retained their outward physical form at 350° C.

The gas yields were low in all cases and the principal constituent of the gas was carbon dioxide. There were lesser amounts of paraffin hydrocarbons. In the experiment with Sample 2, in which two treatments were used, the gas analyses show that the bulk of the carbon dioxide appeared in the first treatment at 250° C. Examination of the pressure-time and pressure-temperature records of all these experiments showed a rapid exothermic reaction near 250° C., during which the pressure rapidly increased 400 to 500 lb. per sq. in. This effect was missing in the second treatment of Sample 2 at 350° C. and in the experiment on Sample 6, in which previously hydrogenated residues were used. The conclusion is that this reaction is accompanied by the release of carbon dioxide.

The amount of water formed was large in all experiments except those in which Samples 4 and 6 were used. In the first case, the low temperature of 300° C. may account for the result, and in the second, the water was probably eliminated in the previous treatments. The low yield of water at 300° C. suggests that the reaction responsible occurs at a temperature considerably higher than that required for the production of carbon dioxide. The high yield obtained in the experiment with Sample 2 may be attributed to the double treatment employed. The water was strongly acidic in all cases, and contained considerable amounts of soluble low-boiling material.

The oils were highly odorous, light yellow and acid in reaction. They were very unstable and darkened rapidly on standing. On distillation, cracking became extensive at or above 200° C. No ultimate analyses of the oils or other products were carried out. However, the oils contained without doubt considerable oxygen. Only about 20% of the oxygen, 5% of the carbon and 10% of the hydrogen content of the screenings were converted to gas and water.

The yield of solid residues was higher than expected, and the result suggests the use of a larger relative amount of tetralin. The best temperature appears to be 350° C. or as an alternative, treatment at 300–325° C. followed by hydrogenation of the residue at 350° C., as with sample No. 6. The double treatment method used with Sample 2 is not effective when compared with a 55.3% over-all conversion to gas and liquid obtained with Samples 4, 5 and 6 in combination.

Semi-continuous Hydrogenations

The apparatus used is shown in Fig. 1. Hydrogen from storage entered through the check valve, A, and stop valve, S, to a surge bottle, B. A pressure gage, C, indicated the pressure in the system. Connection was made to the autoclave, D, through the valve L. The autoclave, of 400 cc. capacity, was placed vertically in a split electric furnace, E, and was fitted at the top end with a column, F, 12 in. long and $\frac{1}{4}$ in. in diameter. The temperature of the autoclave was determined by means of a thermocouple inserted in a well drilled in the wall of the autoclave. Temperature control was automatic to within 5° C. The column, F, was heated by burners operating in

an asbestos jacket, and the temperature was read on the thermometer, R. Manual temperature control was obtained by adjusting the burners. A water-cooled pressure condenser, G, was connected to the expansion valve, H, in a heated oil bath, N. The expanded gases were passed through a condenser in the ice bath J, a flow-meter P and wet test meter K, to a gas-holder.

Weighed quantities of screenings and tetralin were placed in the autoclave, closure was effected, hydrogen admitted until the pressure was about 1000 lb. per sq. in., and the heat turned on. When the temperature was 200° C., hydrogen was admitted at the storage pressure shown in the table, and valves S and L were left open. The expansion valve was opened and adjusted to
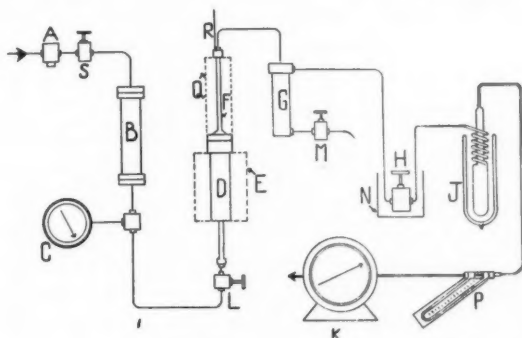
FIG. 1. *Apparatus for hydrogenation in a stream of hydrogen.*

give the desired rate of flow. The column, F, was heated rapidly at the top to the desired temperature. After some definite time, heating was discontinued, valve L closed, and the autoclave was cooled rapidly by opening the furnace. The contents of the pressure condenser.was removed through valve M and weighed together with the contents of the ice condenser, J. The contents of the autoclave was removed as completely as possible, weighed and filtered. The residue in the filter was washed with ether, dried and weighed. The ether washings were heated on a water bath, and the residual oil added to the condensates and filtered oil. A slight loss of volatile material occurred during removal of the ether. The oily material was fractionated as described previously and the aqueous layer fractionated in a micro-distilling column. Both the aqueous layer and oil were strongly acid, and their initial boiling points were between 50° and 60° C. Between 20 and 30% of the aqueous layer boiled below 95° C.

Three experiments, Nos. 57 and 58 on screenings and No. 59 on the combined pitches from Experiments 51 to 58, were carried out with catalysts. In No. 57 a highly active methanol catalyst, consisting of equimolar parts of zinc oxide, copper oxide and aluminium oxide, was used. In Experiments 58 and 59 molybdic oxide was employed. Ten grams of the powdered catalyst was used in each case.

Reference to Table III shows that the losses were high in many cases. The losses were due principally to inability to recover all the contents of the autoclave, and the fact that some of the volatile materials passed through the condenser. The conversions of screenings to solids and water given in Table III are, as a consequence, somewhat low, but the principal losses were associated with the oil. All the loss found was assigned to the screenings, although there is no doubt that part should have been assigned to the medium.

TABLE III

SEMI-CONTINUOUS HYDROGENATION OF GRAIN SCREENINGS IN TETRALIN

Experiment no.	52	53	54	55	56	57	58	59
Tetralin, gm.	60	148	150	150	150	150	150	150
Screenings, gm.	45	50	50	50	50	50	50	50
Temp. of autoclave, °C.	350	350	375	400	400	400	400	425
Temp. of column, °C.	64	65	67	220	215	215	220	235
Operating pressure, lb. /sq. in.	2600	2450	2300	2150	2850	2650	2300	3150
Hydrogen flow, cc./min.	130	120	130	125	180	180	180	185
Time at temperature, min.	40	20	60	60	120	60	60	40
Total off-gas, litres	53.6	15.8	47.2	26.4	46.1	23.0	25.0	19.0
Yields, basis screenings plus tetralin:—								
To solids, %	23.8	12.1	8.0	6.0	4.0	3.5	4.0	0.5
To liquids, %	69.8	83.8	83.0	83.5	84.5	81.5	83.5	92.5
To gases, %	0.7	0.5	0.8	1.1	1.1	0.7	0.7	0.2
To losses, %	5.7	3.4	8.3	9.4	10.4	14.3	11.5	6.8
Conversion of screenings:—								
To solids, %	55.6	48.0	32.0	24.0	16.0	14.0	16.0	1.7
To water layer, %	18.5	23.0	24.0	20.0	24.0	24.0	24.0	3.3
To gas, %	1.6	2.0	3.2	4.4	4.4	2.8	2.8	0.8
To oils, %	11.0	13.5	7.6	14.0	14.0	2.2	11.2	67.0
To losses, %	13.3	13.5	33.2	37.6	41.6	57.0	46.0	27.2
Distillation of liquids:—								
Water layer, %	11.4	7.8	7.7	6.3	7.3	8.3	8.4	1.0
Oil, less 200–206° C. fraction:—								
Over at 175° C., %	1.0	1.3	2.0	3.1	2.8	2.8	1.4	0.5
Over at 225° C., %	5.0	8.5	4.2	5.6	5.6	3.4	4.0	3.2
200–206° C. fraction, %	76.3	76.8	78.7	78.7	77.0	77.3	77.8	74.4
Pitch, %	7.3	6.9	9.4	9.4	10.1	11.0	9.8	21.4
% of water boiling below 95° C.	22.5	25.6	24.0	28.0	30.0	15.0	23.0	—

NOTES:—*Experiment 57—10 gm. of ZnO-CuO-Al₂O₃ catalyst added to charge. Experiments 58 and 59—10 gm. of MoO₃ added to charge. Experiment 59—pitch residues used in place of screenings.*

The tabled values for conversions to oil are as a result highly inaccurate, and it is probable that the sum of the loss and the quantity of oil gives a more nearly correct figure for the conversion to oils. The figures for "solids" are the most accurate.

The physical form of the most resistant constituent, black seeds, was destroyed only at 400° C. In Experiments 52 and 53, the individual seeds, charred of course but of the original shape, could be picked out of the solid residue. In Experiments 54 and 55 at 375° and 400° C., traces of the seeds were evident, but the solid residue was nearly homogeneous and amorphous. In the other experiments, the residues were completely amorphous, and no seeds or seed coats survived destruction.

The variables are numerous and it is difficult to evaluate their effect from the results of the limited number of experiments carried out. The temperature of the column and the rate of gas flow did not appear to have much effect, except in controlling the amount of material collected in the condensers. As it was desirable to remove the more volatile products rapidly, it was found necessary to keep the column head at a temperature of 200° C. or higher. At lower temperatures very little material came over in the gas stream.

The effect of time, temperature and the ratio of tetralin to screenings is shown best in Experiments 52 to 56. In Experiments 52 and 53, an increase in ratio from 1.3 to 3 more than counteracts a decrease in time from 40 to 20 min. Increasing the temperature slightly from 350° to 375° C. and increasing the time to 60 min. in Experiment 54 caused a pronounced decrease in the amount of solid residue. The same beneficial effect of increasing temperature and time is noticeable in Experiments 55 and 56.

The presence of catalysts in Experiments 57 and 58 is of benefit in reducing the amount of solid residue to the same value obtained in Experiment 56, which lasted twice as long. Both catalysts appear to be equally effective and influence the rate of reaction only.

The oils and water recovered in this series of experiments were very similar in properties to those obtained in batch experiments. The pitch residues left at 225° C. were combined and hydrogenated in Experiment 59. The pitches were reduced to a very stable oil, most of which had the same boiling range as the original pitch. The production of water in Experiment 59 shows that the pitches contained oxygen compounds that could be reduced at 425° C., although they were stable at 400° C.

Gas formation in these experiments was slightly less than that found in batch hydrogenation. This is not an unexpected result, in view of the removal of the reaction products from the autoclave as formed. It was interesting to note that the gas formation was less in the presence of the catalysts. A further effect due to the catalysts, but not indicated in the table, was shown by the gas composition, the amount of carbon dioxide produced being less and that of the hydrocarbons being greater, the latter forming the principal constituent of the gas.

In conclusion, it may be said that grain screenings can be reduced very largely to liquids and gases in the presence of an excess of tetralin. About 15% of the screenings remain as solids, and probably 50% or more can be obtained as oils by operation at 400° C. with a 3 to 1 ratio of tetralin to screenings. Comparing the results with similar experiments on cellulose and wood (1), it may be stated that grain screenings are definitely more resistant to reduction under the conditions used. It is highly probable that more effective reduction with the formation of little or no solid residue could be obtained after some further investigation.

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STUDIES OF CARBON BLACK

I. A NEW PROCESS FOR THE PRODUCTION OF CARBON BLACK BY THERMAL DECOMPOSITION OF HYDROCARBON GASES[1]

By L. M. PIDGEON[2]

Abstract

A method is described whereby carbon black is produced from hydrocarbon gases such as methane or propane-butane by thermal decomposition of these gases in a heated tube. The essential feature of the process is the use of a porous refractory tube through which a certain amount of inert gas is allowed to pass. By this means the reacting gas is unable to touch the walls of the system, and deposition of carbon thereon is prevented. Yields as high as 60% of the carbon in the gas, corresponding to 65 lb. per thousand cubic feet, have been obtained from a 70–30 propane-butane mixture, and 19 lb. from methane. The carbon black produced by this process is similar to the "soft" blacks in that it has a high density, low sorptive power, it accelerates the cure in a rubber stock and gives similar resistance to aging and abrasion. It imparts greater stiffness to a rubber stock, however, and in many ways occupies a position between the channel and the "soft" blacks.

Introduction

Carbon black has become one of the most important pigments employed in the rubber industry, as no other substance has been found that will impart similar abrasion resistance to rubber. In spite of the large amounts that are used, the method of production has undergone very little alteration since its inception, and to-day is one of the most wasteful processes known to chemical industry. Most of this carbon black is produced by the impingement of a luminous gas flame on a moving iron plate or other surface, the most common form being a channel section. Subsequent papers in this series will deal with experiments on the preparation of carbon black by the channel process and the relation between the controllable variables and their effect on the properties of the black.

The flame impingement process results in the recovery of not more than 4% of the carbon content of the gas. Such poor yields may be tolerated only where large amounts of natural gas are available, and while there has been the opposite of shortage up to the present time it is quite clear that the situation cannot continue indefinitely, and even now restrictive measures are contemplated or in operation. Much higher recovery of carbon may be obtained by thermal decomposition of the gases in tubes or retorts, but, so far, the carbon produced is distinctly different in type and has had but limited applications. It seems clear, however, that any advances in the methods of production are most likely to be made in this direction. This paper describes the production of carbon black by thermal decomposition of methane and similar gases under conditions such that 60% of the available carbon is

recovered.   The essential point of the process is the use of a porous reaction tube through which some of the heating gases pass, with the object of preventing deposition of carbon on the walls.

There are no theoretical reasons why a gas such as methane could not be decomposed into its elements in such a manner as to recover all the carbon. The decomposition involves the absorption of some 19,000 calories which may readily be supplied by combustion of the resultant hydrogen.   There are a number of practical difficulties, however, that prevent the realization of such yields.

While free energy data indicate that methane is unstable above 575° C. (5), it is known that decomposition is inappreciable below 700°, and even at 1300° in the presence of catalytic surfaces it is incomplete after one hour.   The problem therefore becomes one of design.   It is necessary to develop an apparatus in which a hydrocarbon gas may be subjected to temperatures in excess of 1300° for a time long enough to disintegrate it into its elements, and in such a manner that the carbon may be recovered in a flocculent condition.

It is also essential that the time of contact shall be as short as possible, since it is known from analogy with the flame process that such a condition is required to produce the fine particles that are responsible for the reinforcement of rubber (1, p. 1042).   This limitation necessitates the use of higher temperatures than would be required if thermal decomposition were the only end to be achieved.

These requirements are fulfilled by operation at temperatures so high that a very short contact time is sufficient to disintegrate the molecule into its elements.   However, a very serious practical difficulty arises from the fact that the heat necessary to carry on this endothermic reaction must be supplied through the walls of the reaction chamber, which will be the hottest part of the system and upon which the reaction will be most active.   Any attempt to produce carbon in a heated tube invariably results in the deposition of a layer of carbon on the walls which, owing to its poor heat conductivity, soon insulates the reaction zone from the source of heat.   Furthermore this carbon is deposited in a hard gray, lustrous, condition, and is not useful for the purposes for which carbon black is used.

It is clear that a "wall free" reaction space must be obtained similar to that existing in a flame, in which the heat may be supplied by radiation, since the reacting gas must not touch the walls.   A number of methods, several of which have been so successful as to warrant large-scale operation, have been evolved to overcome this difficulty.

In the "Gastex" (2) process parallel gas streams are employed in such a manner that the hydrocarbon does not touch the walls of the system. Combustion takes place at the air-gas interface supplying the heat to decompose the unburnt hydrocarbon.   This is, in fact, a flame process in which the energy is obtained from flames rather than heated walls.

In the "Thermatomic" process (6) the reaction system consists of a checkerwork of refractory brick which is heated to 1300° C. by gas firing.   The blast

is then shut off and a counter current stream of hydrocarbon is introduced. Cracking takes place and the temperature falls until it becomes necessary to shut off the gas and reheat the brickwork. The deposition of carbon on the walls of this reaction system is of no consequence, as it is burned during the subsequent firing cycle.

Other methods exist involving modifications of the lamp black process, in which smoky flames are produced by suitable adjustment of the gas-air ratio. While any of these methods is theoretically capable of giving high yields of carbon, in practice it is difficult to recover more than 30–40% of the carbon in the gas, a value that is sufficiently good when compared with that of the flame impingement method. The lack of efficiency of the established thermal process methods is in some measure due to difficulty in accurately controlling the reaction. In the parallel gas stream method the presence of turbulence may cause greater admixture of gas and air than is necessary, resulting in loss of carbon. In the Thermatomic process a wide range of temperature is used with varying efficiency, while removal of carbon from the system is not complete.

Thermal Decomposition in Porous Tubes

Since a "wall-free" reaction space is required, it seemed that this could be most readily obtained by the use of a porous tube through which a certain amount of inert gas could be passed to prevent the reacting gas from touching the walls.* This has been accomplished by placing a porous refractory tube in a gas fired furnace in which the pressure was greater than that in the tube. Diffusion of flue gas through the tube supplied on the inside walls, a "blanket", the thickness of which was adjusted by controlling the pressure difference across the walls.

This pressure difference could be produced either by raising the pressure outside the tube (*i.e.*, in the furnace) above atmospheric, or by lowering the pressure in the tube below atmospheric. In experimental equipment it was more convenient to utilize the latter method.

Description of Apparatus

Furnace

The arrangement of the furnace, *A*, is shown in profile and end views in Fig. 1. The lining was constructed of refractory brick insulated with asbestos. The blast was directed against a periclase baffle, *N*, which has proved very satisfactory under somewhat drastic treatment. The pressure within the furnace was indicated on manometer, *C*, and was very slightly above atmospheric. The temperature was measured by means of a platinum–platinum-rhodium thermocouple shielded in a "Pythagoras" tube. When temperatures higher than 1400° C. were encountered an optical pyrometer was employed. Since in all cases the measurements were made outside the tube, the temperature in the reaction zone was probably lower than that indicated, as is

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* *Since this research was completed, the author has noticed Canadian Patent No. 348,990—P. K. Frolich—in which the same principle is involved.*

always the case with an endothermic reaction taking place in refractory tubes of relatively poor heat conductivity. The situation was somewhat improved here by the diffusion of hot gases into the tube at a rate that formed an appreciable fraction of the inlet gas rate. There was also the possibility of exothermic reactions taking place inside the reaction tube.
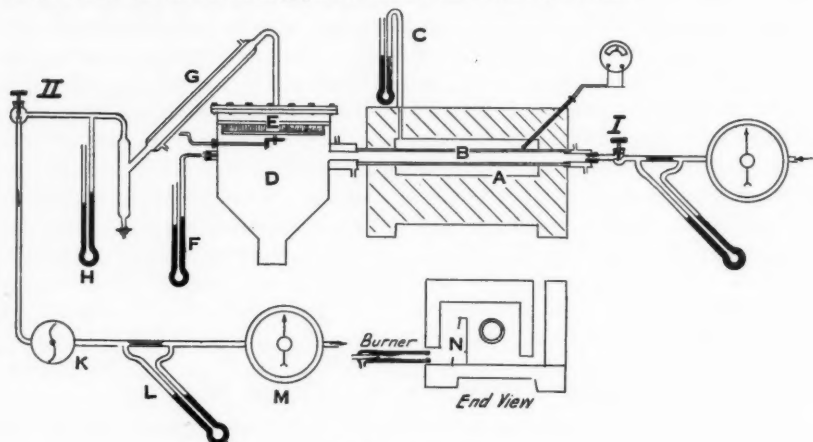
FIG. 1. *Apparatus.*

Porous Tubes

Alundum tubes, *B*, 15 in. in length with an internal diameter of 1 in. and a wall thickness of $\frac{1}{8}$ in. were used exclusively. A coarse alundum (R.A. 90 Norton) which would stand alterations in temperature without fracture was employed. The end portions of tubes which were not in the heated section were painted with sodium silicate to destroy their porosity. The volume of the section heated to the furnace temperature was 0.005 cu. ft. A preheating section of two inches was at a temperature of about 800° C. Gas tight inlet and outlet connections were made by cementing water cooled brass sleeves to the ends with powdered alundum and sodium silicate.

Filter

After leaving the tube, the gas, containing suspended carbon, passed to the filter chamber, *D*, where a measure of cooling was obtained by the use of water cooled baffles. The amount of cooling required careful adjustment, as it was necessary to cool the gas sufficiently to prevent damage to the cloth filter and yet not enough to cause condensation of water vapor, which is an objectionable feature in investigations dealing with carbon black.

The filter, *E*, consisted of a linen cloth backed by a metal gauze clamped between metal rings as shown. It was brushed by rotating the handle as shown at intervals of three to five minutes, depending on the rate of carbon deposition. A motor driven brush was unsuitable, as its use resulted in rapid clogging of the filter. The carbon black fell into the lower part of chamber *D*, and could be removed when desired by opening the bottom of the hopper.

Control of Pressure

After leaving the filter chamber the gas passed through the condenser, G, which removed excess water vapor.   An additional filter (not shown in the diagram) was interposed to entrain any mist of anthracene, tar, etc., that might escape from the condenser.   The outlet rate was controlled by Valve II which checked the pump, K.   This pump was preceded by a tube containing a system of baffles to smooth the gas flow.   The outlet rate and volume were measured at atmospheric pressure with the flowmeter, L, and gas meter, M. The whole system could be controlled by setting Valves I and II.   With I closed and II opened slightly, there was produced in the system B, D, G, a reduced pressure which caused flue gas to enter the reaction space through the porous walls.   The difference in the readings of manometer F and C indicated the pressure difference across the tube.   The amount of flue gas entering the tube (less the water vapor that was condensed in G) could be measured at atmospheric pressure and temperature on the outlet meters L and M.

Each tube was calibrated at the working temperature in order to find the relation between pressure and diffusion rate.   The calibration of a typical tube in the initial condition is shown in Table I.   The results when plotted gave a straight line.   After continued use the tubes became more porous; hence it was necessary to repeat the calibration before each experiment.

TABLE I

POROSITY OF ALUNDUM TUBE AT 1315° C. (VOLUMES AT 76 CM. OF MERCURY AND 25° C.)

Pressure difference, in. of water	1.2	2.0	2.8	3.6
Diffusion per sq. in., cu. ft. per min.	0.0017	0.0028	0.0043	0.0052

From this calibration any desired diffusion rate could be obtained by controlling the pressure difference across the tube.   When the gas to be pyrolized was introduced by opening Valve I, the pressure in the tube B was raised, thereby reducing the pressure difference.   The original pressure was restored by further opening of Valve II.   By adjusting these inlet and outlet rates the required pressure difference could be maintained and with it the desired diffusion rate.

The pressure difference across the filter was indicated by the difference in the readings of manometers F and H.   When this pressure rose above prescribed limits the filter could be returned to its original condition by brushing.

Owing to the changes in volume associated with the reaction, the outlet rate differed from the sum of the diffusion rate and inlet rate, in most cases an expansion having taken place.   As the run proceeded, the inlet rate and the initially established outlet rate were maintained at a constant value by manipulation of the appropriate valves.   Any changes in the porosity of the tube were immediately detectable on the manometer, F.   Deposition of

carbon was shown by the higher pressure required to maintain the same outlet rate, while a sudden fall in pressure denoted a crack in the tube or other leak in the system. The changes in pressure brought about by this procedure are so small (0.5 to 1.6 cm. of mercury) that they exert a negligible effect on the course of the reaction. The composition of the flue gas could be varied within certain limits by altering the gas-air ratio in the blast. The air pressure was carefully controlled with a pressure regulator, and was in the neighborhood of 12 lb. per sq. in. in most cases.

Samples for gas analysis were taken on the outlet side of the condenser unless otherwise indicated. Gas analyses were carried out with a Burrell apparatus of the Orsat type.

Experimental Results

Production of Carbon Black from Methane-ethane

Experiments with methane were made on a natural gas of the following composition: CH_4, 85.1; C_2H_6, 13.5; N_2, 1.4%.

This gas, which may be considered typical of a fairly "lean" natural gas, was pyrolyzed at temperatures between 1350°–1400° C. The amount of diffusion gas required to prevent carbon deposition on the walls at these temperatures could be ascertained only by trial and error; pressures from 2 to 8 in. of water have been employed according to the inlet rate and the tube porosity. Results of experiments on methane appear in Table II.

TABLE II

PRODUCTION OF CARBON BLACK FROM METHANE-ETHANE

Experiment	1	2	3	4	5	6
Pressure, in. of water	6.8	2.4–3.1	1.4	0.2	7.5	1.4
Inlet rate, cu. ft. per min.	0.14	0.08	0.05	0.01	0.06	0.06
Diffusion, cu. ft. per min.	0.23	0.13	0.07	0.02	0.23	0.12
Outlet, cu. ft. per min.	0.40	0.21	0.12	0.04	0.28	0.15
Expansion, %	21	0	0	−100	−16	−50
Temperature, °C.	1360	1380	1380	1380	1390	1390
Yield						
lb. per 1000 cu. ft.	12.8	18.3	17.7	10.7	16.8	18.9
% theory	37	53	51	31	49	55
Apparent time of contact, sec.	0.13	0.25	0.42	1.2	0.18	0.28
Inlet/diffusion	0.6	0.6	0.6	0.6	0.26	0.26

Yield

Yields as high as 60% of theory represent a very good recovery of carbon, and it cannot be said that the possibilities of the method have been fully explored. This yield corresponds to 19 lb. per thousand cubic feet, with which may be compared 3–10 lb. for commercial processes (2).

These yields are based on volume of inlet gas, assuming that the off-gas would provide sufficient heat to operate the furnace. In actual practice, yields would fall short of those stated above by the extent to which it might

be impossible to realize this condition. The validity of the assumption depends so much on furnace design and facilities for heat exchange, both of which factors are impossible to evaluate in an experimental plant, that it appeared better to neglect them altogether.

The yield varies with time of contact, very short times showing poor yields owing to incomplete cracking, while very long times of contact offer greater possibilities for loss of yield by reaction of carbon with the active constituents of the flue gas.

Time of Contact

At 1400° C. the hydrocarbon molecules are almost completely disintegrated into their elements if sufficient time is allowed, yet at shorter times many intermediate compounds may be synthesized. Tropsch and Egloff (7) have shown that the products found by pyrolysis of methane at 1400° C. with very short times of contact are similar to those produced at lower temperatures and with longer contact times. It is clear that in a wide tube the reactions go to varying stages of completeness depending on the space velocity and other factors. The time of contact has therefore been considered as the most important variable at any given temperature, since it controls the amount of synthetic aromatics, tars, etc., and what is perhaps more important, the particle size. The longer the time during which a particle of carbon remains in the cracking zone in presence of unreacted gas and while being subjected to radiation from the heated walls, the larger this particle will become.

In these results the time of contact has been calculated on the assumption that the gas upon entering the furnace was instantly heated to the reaction temperature. An approximate calculation was also made to ascertain the volume of water vapor present in the flue gas as it diffused into the reaction zone. The contact times are therefore more relative than absolute.

Composition of Off-gas

That the mechanism of the decomposition of even the simplest hydrocarbons is a complex phenomenon may be witnessed by the very large literature that exists on the subject. In the present case additional complications are introduced by the presence of the water vapor and oxygen provided by the flue gas. The off-gas will be a complex mixture, the composition of which will depend on the extent to which a number of competing reactions are able to proceed.

TABLE III

COMPOSITION OF OFF-GAS FROM PYROLYSIS OF
METHANE-ETHANE AT 1380° C.

Experiment	Flue gas	1	2
Apparent time of contact, sec.	—	0.13	0.25
Expansion, %	—	21	0
Inlet/diffusion	—	0.6	0.6
CO_2	8.8	3.8	2.0
CO	—	3.8	8.1
O_2	5.1	2.0	2.8
C_2H_2	—	2.1	1.9
Olefines	—	0.4	0.2
H_2	—	23.6	24.4
CH_4	—	8.8	2.6
N_2	86.1	55.5	58.0

TABLE IV

EFFECT OF TIME OF CONTACT ON CONSTITUTION OF OFF-GAS

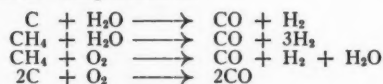| Time of contact, sec.	Expansion, %	CO, %	CH$_4$ (% inlet)	C$_2$H$_2$ (% inlet)	H$_2$ (% inlet)
0.35	−50	7.1	7.4	.7	21.4
0.25	0	8.1	6.3	4.6	59.0
0.17	−16	5.6	16.0	4.7	77.0
0.13	21	3.8	25.0	6.0	67.5
0.10	37	2.8	50.0	5.7	50.0

The composition of the off-gas from several experiments on methane is shown in Tables III and IV. It is perhaps of interest to discuss the possible source of some of the constituents.

Carbon dioxide. The amount of carbon dioxide that has entered the reaction zone as flue gas may be calculated by comparing the nitrogen content of the off-gas with that of the flue gas. Approximate calculations show that in most cases a loss of 20% of the carbon dioxide has taken place. The following reactions proceed actively at 1400° C.,

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$
$$C + CO_2 \longrightarrow 2CO$$
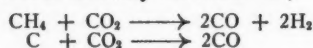
in the direction indicated, and in all probability were taking place to some extent in the present case, resulting in conversion of carbon dioxide to carbon monoxide.

Carbon monoxide. It is clear from the results that some additional reactions producing carbon monoxide are operative, since the percentage of this gas increases steadily with time of contact. The following reactions produce carbon monoxide at these temperatures.

$$C + H_2O \longrightarrow CO + H_2$$
$$CH_4 + H_2O \longrightarrow CO + 3H_2$$
$$CH_4 + O_2 \longrightarrow CO + H_2 + H_2O$$
$$2C + O_2 \longrightarrow 2CO$$

The first two reactions, involving a reduction of water, would result in the production of more carbon monoxide than could be accounted for by the oxygen and carbon dioxide present in the flue gas. An approximate calculation shows that there is less carbon monoxide and carbon dioxide in the off-gas than there should be to account for the oxygen in the flue gas, so that it is unlikely that any reaction involving water is taking place.

It was noticeable that when the time of contact was longer than 0.13 sec. a contraction took place. The only reaction available to cause this is the production of water from hydrogen and oxygen; hence this reaction must be taking place to some extent and may account for the loss of oxygen.

It is desirable to produce an off-gas containing the minimum amount of nitrogen, in order to maintain a high heating value. It is clear that the ultimate possibilities have not been achieved as yet. Alteration in the dimensions of the tube, and operation in vertical position will affect the deposition of carbon, and therefore the diffusion rate that must be employed.

Acetylene.   Yields of acetylene as high as 6%, based on the inlet gas, have been obtained.   The percentage in the outlet gas is, of course, much lower owing to the dilution with nitrogen which is a necessary feature of this process.   This value is close to that reported by Tropsch and Egloff (7), who used much shorter contact times.

Unreacted hydrocarbon.   As shown in Table IV, the percentage of unreacted hydrocarbon falls from 50%, with a contact time of 0.13 sec., to 7% with 0.3 sec.; 0.1 sec. may therefore be regarded as the shortest time that may be reasonably employed at 1380° C.   At very high rates of passage in a tube of the dimensions used, an appreciable portion of the gas may not remain at the decomposing temperature long enough to react.

In order to examine the course of the reaction, a fine silica tube was inserted through the inlet stopper, and gas samples were withdrawn from different positions down the tube.   The gas velocities were adjusted to produce a calculated time of contact of 0.25 sec.   The results, which appear in Table V,

TABLE V

COMPOSITION OF GAS IN VARIOUS POSITIONS IN THE REACTION TUBE

Distance from inlet, in.	2.4	4.8	7.2	11	15 (outlet)
O_2	2.3	1.0	1.2	2.0	2.8
CO_2	1.5	1.7	1.1	1.0	2.0
CO	4.8	2.9	3.1	6.5	8.1
C_2H_2	1.0	3.3	2.5	0.9	1.9
Olefines	2.0	1.3	0.9	0.1	0.2
H_2	10.6	35.4	54.7	42.6	24.4
CH_4	53.2	31.0	12.8	4.2	2.6
N_2	24.6	23.4	23.7	42.7	58.0

show that 50% of the gas had reacted at a distance of 7.2 in. from the inlet; since this point was approximately in the centre of the heated section it represents a time of contact of 0.12 sec.   The production of olefines is very noticeable in the initial stages, but of course these products are destroyed by subsequent heating.   The actual concentration of hydrogen, carbon monoxide, etc., down the tube, appears to fall owing to the increase of the amount of nitrogen obtained from the flue gas.

PRODUCTION OF CARBON BLACK FROM PROPANE-BUTANE

The pyrolysis of a 70-30 mixture of propane-butane has been carried out, using the same apparatus and technique.   The chief difference is the necessity of maintaining a slightly thicker diffusion "blanket" because of the more copious production of carbon made possible by the use of the rich gas.   The results are shown in Table VI, where the various columns have the same significance as in the previous section.

TABLE VI

PRODUCTION OF CARBON BLACK FROM A 70–30 PROPANE-BUTANE MIXTURE

Experiment	7	8	9	10	11	12	13	14
Pressure, in. of water	6.0	6.0	3.0	8.0	8.0	8.4	8.4	8.4
Inlet rate, cu. ft. per min.	0.03	0.06	0.06	0.04	0.06	0.04	0.09	0.20
Diffusion, cu. ft. per min.	0.18	0.18	0.14	0.34	0.34	0.23	0.30	0.29
Outlet, cu. ft. per min.	0.25	0.32	0.27	0.43	0.46	0.35	0.50	0.62
Expansion, %	108	108	130	125	100	200	120	100
Temperature, °C.	1315	1370	1315	1370	1380	1350	1340	1340
Yield,								
lb. per 1000 cu. ft.	62	53	52	69	63	56	—	—
% theory	59	51	50	66	61	54	—	—
Apparent time of contact, sec.	0.20	0.16	0.18	0.10	0.10	0.15	—	—
Inlet/diffusion	0.19	0.32	0.42	0.10	0.17	0.17	—	—

Yield

The appearance of the carbon produced and the percentage recovery are very similar to those found with methane. The actual production is, of course, very much higher, bearing the same relation to the methane production as the ratio of carbon atoms in the two gases (approximately 3.1). The production of any given furnace is unusually high, as values up to 69 lb. per thousand cubic feet have been reported. The same gas when burned in a flame impingement process gave a maximum of 4.9 lb. per thousand cubic feet.

Composition of Off-gas.

Analysis of the off-gas is even more difficult of interpretation than it is with methane, owing to the increased number of possibilities. All the reactions associated with oxygen, carbon dioxide and hydrocarbons are possible and probably take place to some extent. As in the case of methane, there is no evidence of decomposition of water by reaction either with the hydrocarbon or carbon. Considerably higher yields of acetylene have been obtained, as might be expected,—a maximum value of 3.6% in the off-gas was obtained, corresponding to a conversion to acetylene of 22% of the inlet gas.

TABLE VII

COMPOSITION OF OFF-GAS FROM PROPANE-BUTANE PYROLYSIS AT 1325° C.

Inlet rate, cu. ft. per min.	0.03	0.06	0.09
Diffusion rate, cu. ft. per min.	0.13	0.13	0.25
Expansion, %	11	80	111
Apparent time of contact, sec.	0.3	0.2	0.1
CO_2	4.7	2.6	5.0
CO	5.6	3.7	4.9
O_2	1.3	0.5	2.1
C_2H_2	1.1	2.3	3.6
Olefines	0.5	0.5	1.9
H_2	20.0	37.2	19.9
Combustible	2.5	5.2	10.9
N_2	64.6	53.0	51.7
Inlet /diffusion	0.3	0.4	0.3

PREPARATION OF CARBON BLACK FROM A MIXTURE OF ETHYLENE, HYDROGEN AND METHANE

A synthetic mixture of the following composition was made up: hydrogen, 18; methane, 47; ethylene, 35%. This mixture, which contained approximately 38 lb. of carbon per 1000 cu. ft., gave a yield of 21 lb. per 1000 cu. ft.,

corresponding to a recovery of 55%. The general conditions of ope ation and the composition of the off-gas were very similar to those in the case of propane-butane. It appears that approximately 55–60% of the carbon content of any hydrocarbon gas may be recovered. The interest attached to this synthetic gas lies in its similarity to refinery gas and other off-gases from cracking processes.

PHYSICAL PROPERTIES OF CARBON BLACK PRODUCED IN POROUS TUBES

Examination of the physical properties of these carbon blacks has been made from the point of view of their utilization as reinforcing agents for rubber. In order to provide a basis for comparison, similar tests have been carried out on the standard commercial types. Cabots "Spheron" has been selected, as an example of a channel black, and the "soft" blacks have been represented by "Thermax" and "P 33", which is a superior grade of thermatomic carbon.

Appearance

In appearance the new blacks are similar to the thermatomic type. They do not show the intense black color characteristic of a product of the flame impingement process. They are also much more dense and may be readily handled without loss by dusting. The tinting strength is lower than that of the channel black, as also is the oil absorption.

Apparent Density

The apparent density was obtained by tapping a known weight of carbon in a graduated cylinder by means of a motor driven cam, until no further change in volume took place. Prior to this operation the samples were brushed through a 60 mesh screen in order to break up all lumps. The results are considered to have only relative value, as the apparent density values obtained under these conditions are undoubtedly affected by the previous mechanical treatment.

It has been stated as a general rule that the value of a reinforcing agent varies inversely as its apparent density, hence it is desirable to keep this value as low as possible.

If the apparent density is dependent to some extent on particle size, it should also be related to the contact time. In the case of methane a relation was found, as shown in Table VIII. Typical values for channel and Thermatomic black are included for reference, though the results for P 33 and Thermax are not strictly comparable, owing to different initial treatment.

TABLE VIII

Sample	Times of contact, sec.	Apparent density
1	0.42	0.42
2	0.25	0.31
3	0.13	0.24
Thermax	—	0.5
P 33	—	0.4
Uncompressed channel	—	0.1

Since a high apparent density is related to a large particle size, it seemed that this could be affected by diluting the inlet gas, a procedure that should tend to prevent the production of large particles. This process is commercially employed in the Thermatomic process (4), and results in the production of a superior grade of "soft" black.

The effect of diluting the input gas with hydrogen is shown in Table IX, where it is seen that the apparent density of the black has been decreased by this treatment. This dilution is accompanied by a loss in yield. Drogin (2)

TABLE IX

Inlet rate, cu. ft. per min.	Diffusion rate, cu. ft./min.	Outlet rate, cu. ft. per min.	% Hydrogen	Yield, lb. per 1000 cu. ft.	Apparent density
0.14	0.23	0.285	0	12.8	0.24
0.15	0.18	0.30	50	10.0	0.21
0.18	0.20	0.375	50	7.6	0.15
0.2	0.20	0.375	75	4.4	0.12
Channel black	—	—	—	1.4	0.10

NOTE:—*Temperature, 1355° C.*

suggests that in the case of thermal process blacks the lower the yield, the nearer do the physical properties of the product approach those of a channel black, a statement that is well borne out in Table IX.

The effect of contact time on apparent density was less evident with propane-butane than with methane, perhaps because of the dilution effect, which may be more important in the latter case.

Sorption

The sorptive power of a rubber filler is an important physical property, since it is generally considered that a high sorption produces a retarded cure, either by removal of the accelerator or some other reactant. A number of sorption tests, among which may be mentioned the use of methylene blue, iodine and diphenyl guanidine, have been utilized to evaluate this property. Methylene blue was chosen in the present case because of the ease and rapidity with which the measurements may be made by colorimetric methods. The experimental technique is of the simplest nature, consisting of shaking the carbon with a solution of the sorbate in a suitable solvent. The amount taken up by the black is obtained by ascertaining the concentration after filtration, or centrifuging.

TABLE X

SORPTION OF METHYLENE BLUE BY CARBON BLACKS*

Time of contact, sec.	Sorption, mg./gm.
Methane { 0.13	4.4
0.25	3.6
0.4	4.4
1.2	2.4
Propane { 0.2	8.4
0.1	14.2
Diluted methane, 0.1	20.8
Thermax (Thermatomic)	4.4
Cabots (Channel)	33.6

*0.25 gm. carbon shaken for 1 hr. with 50 cc. of .025% aqueous methylene blue solution.

As shown in Table X, the new blacks do not absorb appreciable amounts of the dye.   The sorptive power of the average sample of methane black is similar to that shown by Thermax.   Propane blacks showed higher sorptive power, while the black made from the mixture of hydrogen and methane showed sorptive power comparable with that of the channel black.   This may be considered as a further indication of the effect of dilution on particle size.

In general, thermal process blacks do not retard the rubber cure, in fact an accelerating effect is noticed.   This behavior is also characteristic of the new blacks, as will be seen presently.

Volatile

The production of carbon by thermal decomposition of a hydrocarbon gas is accompanied by the usual decomposition and polymerization reactions which always take place under these conditions.   While no quantitative determinations have been made, it was obvious that appreciable amounts of naphthalene, anthracene, and tars of unknown constitution were being formed in the tube.   This was particularly noticeable at high gas velocities, when the time of contact was too short to permit complete cracking of the hydrocarbons to take place.

A certain amount of these polymerized bodies is absorbed on the carbon black, and is classed as volatile matter.   Determinations carried out in the usual manner by heating the carbon black for seven minutes at 950° C. indicate a volatile content ranging from 0.5 to 2%, depending on the time of contact and on the temperature of the filtering system.   Under special circumstances values as high as 16% were found.   All the samples that have been used for rubber tests gave values lower than 1%.

The chemical constitution of the volatile matter is different from that of a channel black, consisting as it does of aromatic material, much of which may be distilled off at relatively low temperatures.   The volatile constituents of channel black must consist of material that is stable at 400° C., as this is the temperature of the steel channel on which the black remains for some time. Volatile constituents of the thermal process blacks are composed of polycyclic compounds of the anthracene type, many of which may be distilled off at 400 C.

It was not proved that the volatile content exerted any effect on the ease of dispersion or the reinforcing properties of the blacks.   High volatile contents have been shown (4) to be an undesirable feature of channel blacks, but the situation is so different here that it is doubtful whether any analogy exists. The "soft" blacks may be very readily dispersed in rubber in any case (3), while one rubber test carried out on a sample that had been freed of volatile matter by heating to 950° C. showed no appreciable difference in reinforcing power.

Tensile Tests   REINFORCEMENT OF RUBBER

Rubber tests have been carried out according to the usual methods.   The following basal formula was employed: Smoked sheets, 100 parts; zinc oxide, 3; stearic acid, 2; sulphur, 5; diphenyl guanidine, 0.75.   To this was added—

carbon, 35. The mixes were made up in a laboratory mill, and they were then vulcanized in a four cavity mold in a steam press at 141.5° C. for various times, as shown in the tables. Tensile tests were carried out with dumb-bell test pieces.

Carbon black from methane. Results of rubber tests carried out on carbon black produced from methane are shown in Table XI.

TABLE XI

TENSILE PROPERTIES OF PURE GUM RUBBER AND RUBBER CONTAINING CARBON BLACK FROM METHANE (KG. PER CM.^{2})

Cure, min.	Modulus at elongation of					Ultimate tensile	Ultimate elongation	Hardness (Shore)
	200%	300%	400%	500%	600%			
Pure gum								
35	—	—	13.3	19.1	29.1	62.5	1000	36
55	—	13.3	20.3	27.3	54.6	100	775	37
75	—	17.1	22.7	39.0	67.4	176	765	41
95	13.7	20.1	28.5	45.1	92.5	216	730	44
Methane blacks								
Sample 1. Calculated time of contact, 0.13 sec.								
35	17.2	32.7	60.0	105	164	225	700	44
55	24.4	45.0	83.0	134	208	263	675	51
75	32.0	61.5	106	168	255	269	612	53
95	34.9	68.0	117	172	259	265	602	56
Sample 2. Calculated time of contact, 0.25 sec.								
35	16.8	30.2	54.0	96.6	151	204	690	47
55	23.4	42.0	76.5	129	200	243	650	49
75	29.0	53.0	100	150	230	254	630	52
95	33.4	61.0	102	167	—	250	600	53
Sample 3. Calculated time of contact, 0.42 sec.								
35	15.0	29.2	52.0	91.0	145	197	665	43
55	21.2	41.5	75.0	126	187	227	640	47
75	25.8	50.9	94.0	154	228	235	615	52
95	32.8	63.0	112	179	—	235	580	54

The results in Table XI are plotted in Figs. 2 and 3, together with values for "P 33", Thermax and a standard channel black. It is apparent that the tensile properties of the new blacks place them between P 33 and the channel blacks. If the stiffness of the channel black rubber at 500% elongation is considered as 100, that of P 33 is 64, and that of the blacks under discussion ranges from 75 to 85. The ultimate tensile is essentially the same as that of P 33, and therefore slightly lower than that of a good channel black.

The rate of cure is quite different from that for the channel black and very similar to that for the Thermatomic black, as shown in Fig. 3. It is clear from
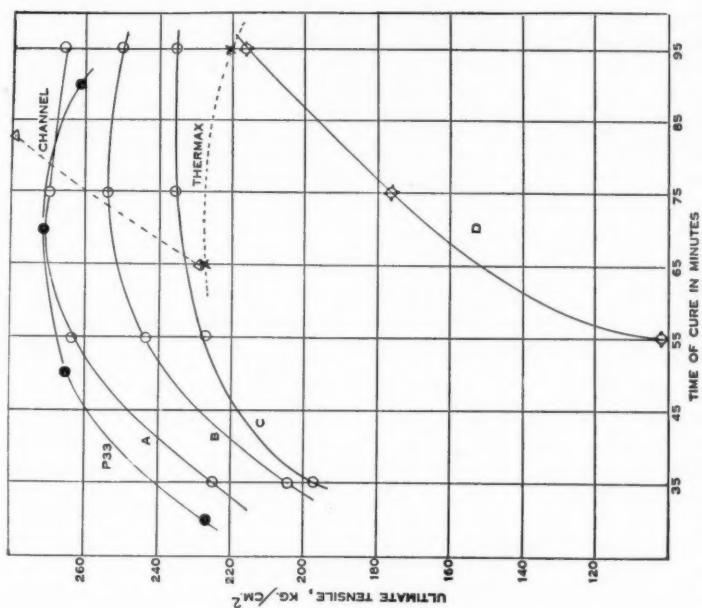
FIG. 3. *Rate of cure. A, B, C—carbon black from methane; apparent time of contact—A, 0.13 sec.; B, 0.25 sec.; C, 0.42 sec. D, pure gum.*
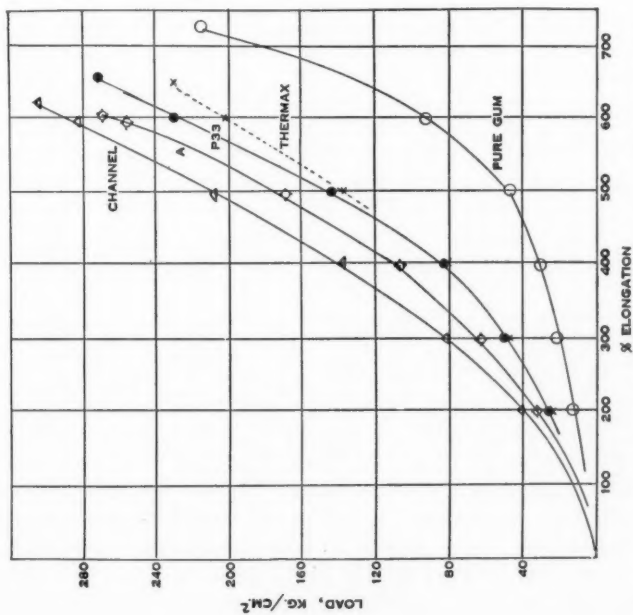
FIG. 2. *Stress-strain relation at optimum cure. A, Carbon black from methane.*

the results that on this score the new blacks fall into the Thermatomic class; as already pointed out they have very little sorptive power, and it is evident that they actually exert an accelerating effect on the cure, as shown in Fig. 3, where it is seen that the pure gum sample is definitely undercured at 75 min., a time that produced the maximum tensile strength in these blacks. The optimum cures for pure gum and a channel black compound were from 100 to 105 min. when this formula was used.

A definite relation between contact time and rubber reinforcement was found with methane, following the same order as the apparent density relations. Again the propane-butane samples did not show such a definite relation between contact time and reinforcement, in common with the irregularities which had already been noted in the apparent density measurements.

Carbon black from propane-butane. It has been shown that the theoretical yield and general characteristics of the carbon produced from propane-butane are similar to those of the carbon produced from methane. This similarity also extends to the reinforcing power of these blacks, as will be seen in Table XII, where the results of a number of rubber tests are shown which do not differ essentially from those found for the black produced from methane.

TABLE XII

TENSILE PROPERTIES OF RUBBER CONTAINING CARBON BLACK FROM
PROPANE-BUTANE AND "P 33" (KG./CM.^{2})

Cure, min.	Modulus at elongation of					Ultimate tensile	Ultimate elongation	Hardness (Shore)
	200%	300%	400%	500%	600%			
Propane-butane								
Calculated time of contact, 0.1 sec.								
30	17.2	31.2	63.9	109	166	179	620	41
50	26.6	59.2	108	173	—	241	600	52
70	30.6	64.5	115	188	258	258	600	52
90	31.6	69.2	126	197	265	265	600	53
Calculated time of contact, 0.3 sec.								
30	17.9	33.3	60.3	96	151	193	550	41
50	28.7	55.7	89.5	147	217	245	620	52
70	33.6	61.5	102	168	246	246	600	56
90	36.9	68.9	110	179	—	247	595	56
"P 33"								
30	16.0	23.0	37.0	72.0	135	226	720	47
50	24.5	42.0	74.0	127	205	266	680	57
70	28.5	50.0	81.3	144	232	271	640	55
90	31.2	49.8	83.8	143	232	262	620	56

Aging test. Test pieces were milled and vulcanized in such a manner as to produce both an overcure and an undercure. In order to obtain comparative results a sample was prepared using Cabot's "Spheron". The same formula and curing temperature as used in the tensile tests were employed.

Two dumb-bell test pieces from each slab were tested immediately, and the remainder were placed in an oven at 70° C. for eight days. Air circulation was maintained throughout this period by means of a fan, and a certain amount

of fresh air was continuously drawn into the oven.   At the end of this time the samples were tested in the usual manner.   The results are shown in Table XIII, where it is seen that the new blacks exhibit the property of

TABLE XIII

RESISTANCE TO AGING

Modulus at	Original	Aged	% Original	Modulus at	Original	Aged	% Original
F27–47 min. cure				**Cabot's Spheron—100 min. cure**			
300	57.2	62.0	108	300	82	—	—
500	163	151	92	500	209	—	—
Ultimate tensile	285	212	74	Ultimate tensile	301	45.9	15
Ultimate elongation	656	590	90	Ultimate elongation	640	170	27
F27–70 min. cure				**Cabot's Spheron—125 min. cure**			
300	72.9	90.0	125	300	86	—	—
500	195	—	—	500	215	—	—
Ultimate tensile	279	153	55	Ultimate tensile	301	45.0	15
Ultimate elongation	610	425	70	Ultimate elongation	615	150	24
P33–50 min. cure (original), 47 min. cure (aged)							
300	42.0	40.2	95				
500	127	109	86				
Ultimate tensile	266	186	70				
Ultimate elongation	680	636	93				

retarding aging which is characteristic of thermatomic blacks.   The above treatment destroyed the channel black samples but left the new blacks in reasonably good condition.   Resistance to aging is similar to that shown by "P 33" which has been stated to give better resistance than that given by any other ordinary filler (8).

Abrasion Tests

Resistance to abrasion is the most important characteristic of carbon black rubber, and the one that has placed this pigment in its dominant position. This property was examined on the Dupont abrader.   Various samples of the same D.P.G. formula were vulcanized in the special mold provided with the machine.   Tests were carried out in the usual way, the results being expressed as the loss of volume in cubic centimetres per horsepower hour.

The new blacks are slightly superior to P 33 but considerably inferior to the channel black, as seen in Table XIV.

TABLE XIV

RESISTANCE TO ABRASION

Sample	Cure time, min.	Loss, in cc. per h.p. hour	Reciprocal × 1000
F 27	30	346	2.9
	50	249	4.0
	70	229	4.4
P 33	30	465	2.2
	50	283	3.5
	70	247	4.0
"Spheron"	85	180	5.6
	100	184	5.4
	120	169	5.9

Conclusion

It has been shown that hydrocarbon gases may be decomposed to carbon and hydrogen in a heated tube in a continuous process, if the walls of this tube are porous and if a certain amount of inert gas is passed through.   The pyrolysis reaction, therefore, takes place in a "wall-free" space.   The efficacy of this method was shown in a striking manner by approximately one minute's operation without diffusion.   In this short time the tube became heavily coated with carbon.

When methane is treated under these conditions at temperatures between 1300° and 1400° C., it is decomposed into its elements in such a manner that 60% of the carbon in the gas may be recovered.   In the experiments that have been described, the inert blanket was composed of flue gas consisting of water, carbon dioxide, nitrogen and some excess oxygen.   A certain amount of reaction takes place between this gas and the methane and carbon black, resulting in loss of yield.   It seems that it should be possible to improve the method considerably, when all the details are worked out.   The amount of gas diffusing through the walls required to prevent carbon decomposition depends on so many factors that it must be ascertained by trial and error.   The average thickness of the diffusion layer calculated from the volume ratios is 0.2 in.   It follows therefore that the blanket occupied at least one-half of the volume of the tube.   With larger tubes, different space velocities, and possibly operation in the vertical position, this ratio might be considerably improved.   Reduction in the amount of flue gas added through the walls would have the further desirable feature of producing an off-gas of higher calorific value.

While the carbon black that is produced by this process shows properties very similar to those of the thermatomic black, it possesses a number of individual features.   The stiffness produced in a rubber stock is intermediate between that of the channel and that of the commercial thermal type, while oil absorption and blackness are somewhat higher than those of the thermal type.   The effect of gas dilution on the properties of the resultant black has not been worked out in detail, but the increase of sorptive power suggests a smaller particle size which should be reflected by superior rubber reinforcement.

Since the carbon black produced by flame impingement exhibits the optimum reinforcing action, it seems that a black of comparable properties may be produced only by imitating in some measure the conditions that exist in the flame, that is, a very high temperature (about 1800° C.) and a very short time of contact, followed by rapid cooling to a temperature below that of reaction. It is doubtful whether these conditions may ever be completely realized, except where a flame plays on a cool surface.

Acknowledgments

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STUDIES IN THE SYSTEM
CALCIUM-OXIDE–SULPHUR-DIOXIDE–WATER

III. PRECIPITATION TEMPERATURES[1]

By P. E. Gishler[2] and O. Maass[3]

Abstract

A technique is described for measuring the precipitation temperatures of the system calcium-oxide–sulphur-dioxide–water, and the results over a considerable concentration range are tabulated. It is shown that the presence of colloidal matter brings about a condition of supersaturation. The hydrogen ion and bisulphite ion concentrations for the solutions at the precipitation temperature have been calculated. It is suggested that the hydrogen ion concentration plays an important role in precipitation, and the copious nature of the precipitation with rising temperature above the precipitation temperature is explained.

A table containing bisulphite ion concentrations over a large range of calcium oxide and sulphur dioxide concentrations, and over the temperature range 50–90° C., is given. It is pointed out that the system calcium-oxide–sulphur-dioxide–water acts as a buffer solution so far as bisulphite ions are concerned.

Introduction

For each concentration of calcium oxide and sulphur dioxide, there is a temperature at which a precipitate is formed. When precipitation occurs it is usually copious, and this is believed to be due to the tendency of this system towards supersaturation. The precipitate has been found to be calcium sulphite. Precipitation is somewhat similar to that which occurs in the system $Na_2SO_4 . 10H_2O$ at 33° C. (1) and $CaSO_4 . 2H_2O$ at 63.5° C. (4), only that it is more complicated by the fact that in this case the system is a three component one, and the sulphur dioxide, as well as the calcium oxide, concentration determine the precipitation temperature. Three concentrations of calcium oxide were studied, i.e., 0.6, 1.2 and 2.0%. For each of these calcium oxide concentrations the influence of five different sulphur dioxide concentrations was investigated.

Experimental

Glass bombs were filled with accurately known amounts of calcium oxide, water and sulphur dioxide. They were then sealed from the measuring apparatus, and shaken in a bath in which the temperature of precipitation was determined. The bombs were made of 1 in. Pyrex glass, and were about six inches in length. A $\frac{1}{4}$ in. tube sealed into the side of the bomb served for the introduction of pure calcium oxide and water. The top of the bomb contained a stem, which was sealed to the evacuation and gas measuring system.

Fig. 1 shows the apparatus used for determining precipitation temperatures. A bath of dibutyl phthalate containing the necessary heaters, stirrers and cooler served to maintain the bombs at any desired temperature.   The bombs were clamped to a rotating wheel which served as an agitator.

The apparatus for filling the bombs was so built that five could be filled at a time.   After the bombs were made and cleaned they were sealed to a manifold, which was attached to the evacuation and gas measuring system. They were evacuated and then filled with dry air free from carbon dioxide. The side arm was broken open and a weighed amount of calcium oxide introduced. The desired amount of water was then pipetted into each bomb, and the side arms were sealed off near each bomb.   The next step involved the removal of dissolved gases.   The stopcocks leading from each bomb to the manifold were closed and the manifold evacuated. Each stopcock was rapidly turned several times in order to remove the air from the space above the water in the bombs.   As the pressure was reduced, air was seen to bubble from

Fig. 1.   *Apparatus for determining precipitation temperatures.*

the water.   This was removed at intervals until all dissolved gases were displaced.   The loss of water by evaporation was slight.

Sulphur dioxide was purified, measured and introduced by a slight modification of the method described in detail in a previous paper (3).   The apparatus used was that employed in the earlier investigation (3).   The desired amount of sulphur dioxide was condensed from a high pressure storage cylinder into a glass bulb.   Three redistillations with rejection of the upper and lower fractions yielded pure sulphur dioxide.   This was measured in bulbs of known volume which were attached to a two armed manometer.   After the pressure and temperature had been determined, the gas was allowed to flow into one of the bombs, in which it went slowly into solution.   The rate of solution could be followed by observing the change of pressure on the manometer.   When the desired amount of sulphur dioxide had been passed into the bomb, it was sealed off and thoroughly shaken in order to dissolve the calcium oxide present.   Any sulphur dioxide remaining in the manifold and connecting tubing was condensed back into the measuring system.   It was therefore possible to determine accurately the amount of sulphur dioxide in the bombs.
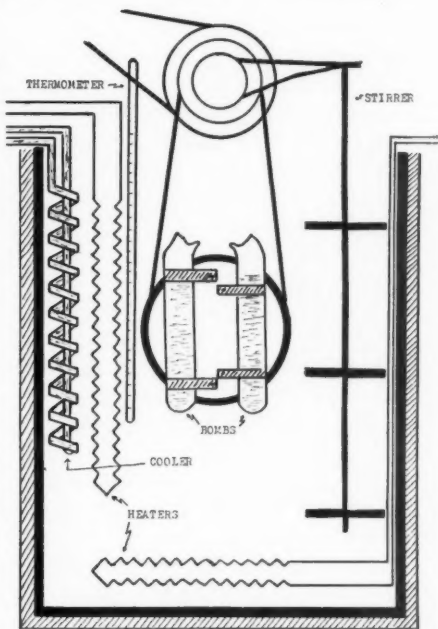
Two bombs were clamped simultaneously to the vertical rotating wheel in the bath. During rotation the solutions splashed from end to end of the bombs, thus ensuring thorough mixing. Precipitation temperatures were determined by approximation. The bombs were heated up rapidly, and as precipitate was observed to form in each bomb the temperature was noted. Under these conditions supersaturation was unavoidable, and precipitation, once started, was heavy. The bath was then rapidly cooled down until the precipitate in both bombs had dissolved. Each bomb was then considered separately. Several test experiments had shown that, under conditions of rapid heating, supersaturation of more than 15° C. could occur. The object was to find the lowest temperature at which a solution of given concentration would precipitate.

The bomb was heated to within 15° C. of the previous precipitation temperature and held there for an hour. If precipitation did not occur at that temperature, the bomb was heated up at a rate of about 2° C. per hour until precipitation did occur. This was not considered as the precipitation temperature but as a reasonable approach to it. Several similar attempts were made to ascertain whether precipitation could be induced at a lower temperature. Eventually a temperature was reached below which precipitation would not take place.

At a temperature just below this one it should have been possible to bring the calcium sulphite into solution. There was one great difficulty involved and that was the time factor. It was found that at 15° C. below the apparent precipitation temperature, it was possible within a reasonable time (three to four hours) to bring the solid into solution, but at 10° C. below that temperature the time factor increased tremendously.

Results

Seventeen different concentrations were studied. These were divided into four series. Series A consisted of solutions of six different concentrations of sulphur dioxide in which there was 1.2 gm. of calcium oxide per 100 gm. of water, the sulphur dioxide concentrations varying from 1.9 to 6.7%. The solutions in the five bombs of Series B contained 2% of calcium oxide, and the sulphur dioxide concentrations varied from 3.6 to 6.6%. In the six bombs of Series C were solutions containing 0.6% of calcium oxide and from 1.2% to 5% of SO_2. However, the contents of bombs No. 4 to No. 6 could not be successfully studied. A trial test with No. 4 showed that calcium sulphite could not be made to precipitate even at 152° C., and the apparatus was not constructed for high temperature work. Series D was a repetition of B, except that the bombs also contained 0.5% of a peptizing reagent. This tended to raise the precipitation temperature.

The results are shown in Table I and in Fig. 2, in which the temperature is plotted against sulphur dioxide concentration. The points fall on a smooth curve, except 3A which is an example of persistent supersaturation. The best means of illustrating this supersaturation is to include a detailed description of an experiment as made in the laboratory.

TABLE I
PRECIPITATION TEMPERATURES

	Vol. H_2O, cc.	Wt. CaO, gm.	Wt. SO_2, gm.	% SO_2	Ratio SO_2/CaO	Precipitation temp., °C.
A 1	50	0.600	0.966	1.87	1.41	50.5
2	25	0.300	0.814	3.29	2.44	97.0
3	50	0.600	2.282	4.32	3.33	117.0
4	50	0.600	2.531	4.76	3.69	117.0
5	25	0.300	1.558	5.78	4.50	135.0
6	25	0.300	1.822	6.72	5.27	137.0
B 1	25	0.500	0.965	3.64	1.69	45.0
2	25	0.500	1.091	4.09	1.91	75.7
3	25	0.500	1.411	5.25	2.47	93.0
4	25	0.499	1.644	6.07	2.88	103.5
5	25	0.495	1.802	6.60	3.18	107.5
C 1	25	0.151	0.311	1.22	1.82	100.0
2	25	0.150	0.352	1.38	2.06	116.0
3	25	0.150	0.377	1.48	2.20	130.0
4	25	0.150	0.750	2.89	4.38	152.0*
D 1	25	0.501	1.330	4.96	2.32	117.8
2	25	0.498	1.192	4.45	2.10	95.5
Precipitation results from conductivity data						
	84.26	0.99	2.70	3.08	2.38	95
	88.29	2.06	5.30	5.56	2.25	57
	88.29	2.06	6.80	7.00	2.88	65

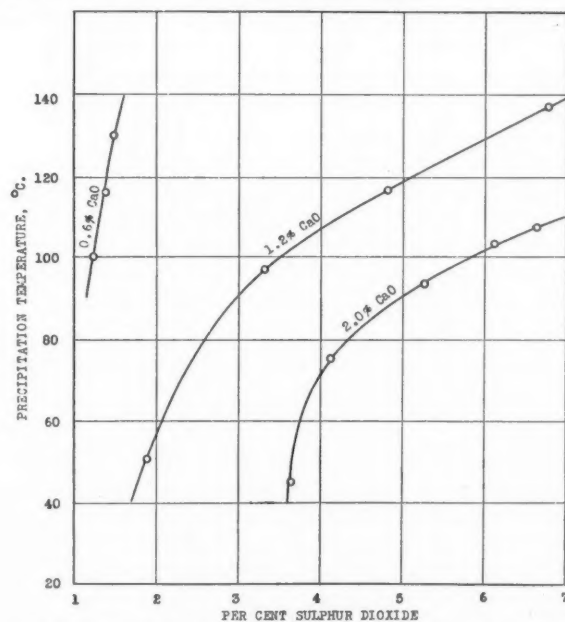*Solution was heated to 152° C. but no precipitation took place.

FIG. 2.   Precipitation temperatures of the system calcium-oxide–sulphur-dioxide–water.

"Bombs No. 2A and No. 3A were clamped on the wheel and rapidly heated until a precipitate began to form in 2A at 109° C. The temperature was held at this point and soon a heavy precipitate was formed. It consisted of large white flakes of calcium sulphite. The bath was heated to 127° C. but a precipitate did not form in No. 3A. The bath was cooled down until the precipitate in No. 2A dissolved. It was again heated slowly and at 102° C. a precipitate was formed. It was cooled down and at 74° C. the precipitate had completely dissolved. The bath was heated to 95° C. and then very slowly to 97° C., at which temperature a slight precipitate formed. The solid was once more brought into solution by cooling, and then the bath was heated to 90° C., after which it was heated at the rate of 1° C. per hour. It was held at 93° C. for an hour, but precipitation did not take place. No solid was formed until the temperature was raised to 97° C. On heating to temperatures higher than this, the amount of precipitate increased rapidly with rise in temperature." A similar procedure with No. 3A yielded the following series of precipitation temperatures; 135°, 123°, 118° and 117° C. After precipitation, No. 3A was held at 105° C. for three hours, and it could be noticed that very little of the precipitate dissolved.

One experiment was carried out in an apparatus described in a previous paper (3), the object being to determine quantitatively the change in vapor pressure that takes place owing to precipitation. The results are shown graphically in Fig. 3. A solution containing 88.294 gm. of water, 2.061 gm.
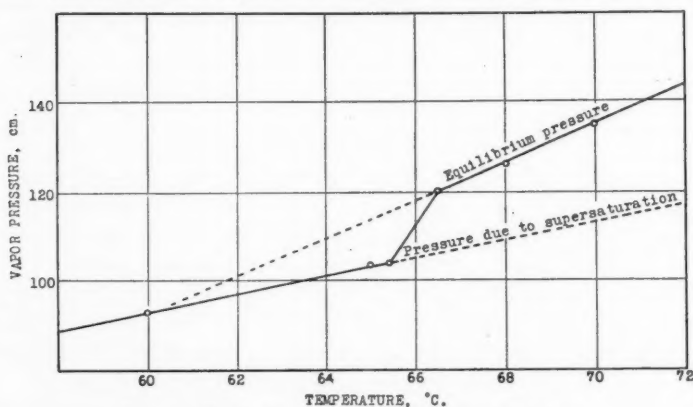

FIG. 3.　*Vapor pressure changes due to precipitation.*

of calcium oxide and 6.845 gm. of sulphur dioxide, was heated until precipitation occurred at 75° C. Vapor pressure determinations were not made in this preliminary test, since time had not been allowed for the solution to reach equilibrium before the precipitation temperature was reached. The mixture was cooled in order to bring all solid into solution. The cell was then slowly heated to 60° C., at which temperature it was held until equilibrium

was established. A vapor pressure determination was then made. The cell was then heated slowly to 65° C. and the temperature was held constant until equilibrium was established, after which a vapor pressure determination was made. At 65.4° C., a precipitate began to form. The cell was held at 66.5° C. until the vapor pressure became constant. Vapor pressure determinations were made at 66.5, 68 and 70° C.

A copious precipitate was formed at 65.4° C., indicating that the solution was supersaturated at that temperature. It was possible to calculate the degree of supersaturation. In a previous paper (3), the data obtained on the rise in pressure due to a decrease in calcium oxide concentration was presented in tabular form. In Fig. 3 the temperature range covered is so small that straight line extrapolation is permissible. The true precipitation temperature was found by extrapolation to be 60.4° C. It is believed that, under the proper conditions of heat treatment, precipitation could be made to occur at any temperature above 60.4° C. If precipitation were made to take place at 70° C., the vapor pressure before precipitation was 113 cm. The vapor pressure after precipitation to an equilibrium value is 135 cm. The increase of pressure is due to the removal of a definite amount of calcium sulphite from solution. Since vapor pressures of the system calcium-oxide–sulphur-dioxide–water are known over a wide temperature and concentration range (3), it was possible to calculate the amount of calcium sulphite that it is necessary to remove in order to produce a pressure increase of 22 cm. It was found that, under the conditions described above, approximately 0.5 gm. calcium oxide was removed as calcium sulphite. Thus it is seen that in a rise of only 10° C. above the precipitation temperature, a quarter of the total calcium has been precipitated as calcium sulphite. In Fig. 3 the vapor pressure curve of the system after precipitation has been extrapolated back to cut the pre-precipitation curve at the true precipitation temperature. Had no supersaturation occurred, there would have been very little solid formed at 60.4° C. As the temperature is raised however the amount of precipitate increases, the quantity depending upon the difference between the vapor pressure represented by the upper, and that by the lower, curve.

Another quantitative method of studying precipitation is apparent from a consideration of the conductivity data (3) of this system. If a solution containing calcium oxide and sufficient sulphur dioxide to completely dissolve it is heated, the specific conductivity increases in a regular manner with increase in temperature. At the precipitation temperature, however, there is a sudden break in the curve, and with further increase in temperature the specific conductivity decreases in a regular manner. If precipitation takes place above the true precipitation temperature, the curve will take the form shown in Fig. 4. At any temperature above the precipitation temperature, the difference in conductivity represented by the first, and that by the second, part of the curve is a measure of the amount of supersaturation at that point.
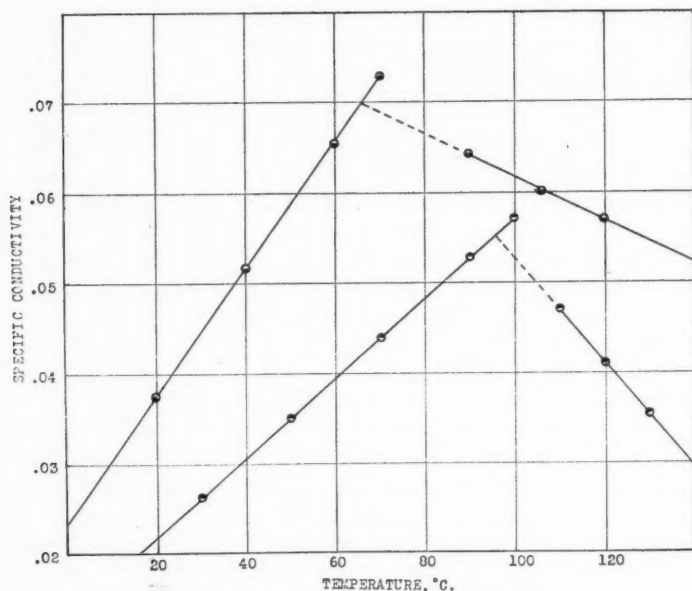
FIG. 4.   *Conductivity in the precipitation region.*

Discussion

The precipitation temperatures for various concentrations of the system calcium-oxide–sulphur-dioxide–water have been determined directly in the manner described in this paper. Two other methods of measuring the precipitation temperature have been discussed, namely, by means of data on vapor pressure and conductivity discontinuities. The values deduced from the last two are, within experimental error, in complete agreement with the direct determinations.

There are two striking features connected with the precipitations. One is the tendency towards supersaturation, and the other, the apparent volume of precipitation that occurs when the temperature exceeds the true precipitation temperature. In regard to the first, the time factor seemingly plays an important role. If a solution is heated rapidly, it is easily possible to raise the temperature above the precipitation temperature without the formation of a precipitate of calcium sulphite, and it seems that the rate of rise in temperature above the true precipitation temperature plays an important part in the formation of solid. Furthermore, the presence of colloidal matter seemingly inhibits the precipitation of solid. Consequently, the temperatures as listed in this paper would in all probability be greatly exceeded when the same system is heated in the presence of wood.

In regard to the copious precipitation that takes place with rise in temperature, once it starts it might well be that precipitation is dependent on a change in hydrogen ion concentration. To determine the effect of hydrogen

ion concentration, the concentrations at the precipitation temperatures have been calculated by the method described in a previous paper (2). Table II shows the relation between hydrogen ion concentration and concentration of the solution at the precipitation temperature.

The data in Table II are presented graphically in Fig. 5, each curve representing a constant sulphur dioxide concentration and varying calcium oxide content. It is seen that, in order to prevent precipitation, the concentration of

TABLE II

HYDROGEN ION CONCENTRATION AT WHICH PRECIPITATION OCCURS

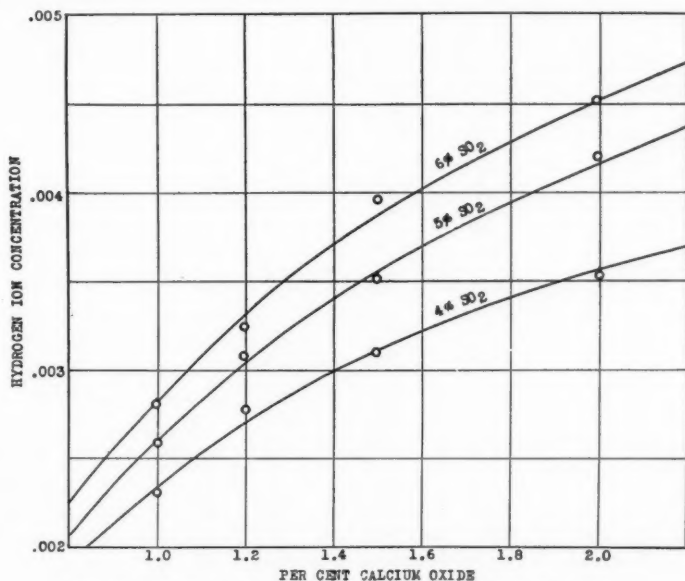| %SO$_2$	2% CaO		1.5% CaO		1.2% CaO		1.0% CaO	
	Temp., °C.	[H+]	Temp., °C.	[H+]	Temp., °C.	[H+]	Temp., °C.	[H+]
4	70	0.0035	92	0.0031	107	0.0028	114	0.0023
5	92	.0043	108	.0035	118	.0031	125	.0026
6	102	.0045	119	.0040	130	.0032	136	.0028

FIG. 5. *Hydrogen ion concentration in the precipitation region.*

hydrogen ions must be increased with increase in calcium content. The limits of hydrogen ion concentration are not very large over the whole range of calcium oxide concentrations studied, the largest variation being only 100%. Evidently a hydrogen ion concentration within a relatively narrow range will keep the calcium in solution.

The bisulphite ion concentrations were calculated for the solutions at their precipitation temperatures, and were found to vary by an insignificant amount. In Table III the values at the precipitation temperatures are given for 1, 1.2, 1.5 and 2% of calcium oxide.

TABLE III

BISULPHITE ION CONCENTRATION AT WHICH PRECIPITATION OCCURS

% SO.	2% CaO		1.5% CaO		1.2% CaO		1.0% CaO	
	Temp., °C.	[HSO$_3$-]	Temp., °C.	[HSO$_3$-]	Temp., °C.	[HSO$_3$-]	Temp., °C.	[HSO$_3$-]
4	70	0.177	92	0.177	107	0.170	114	0.167
5	92	.175	108	.156	118	.159	125	.158
6	102	.172	119	.150	130	.147	136	.152

This constancy of bisulphite ion concentration is not limited to the precipitation temperatures. To show this, the bisulphite ion concentrations over the complete concentration range at temperatures of 50°, 70° and 90° C. were calculated and are shown in Table IV.

TABLE IV

BISULPHITE ION CONCENTRATIONS

% CaO	% SO$_2$	50° C.	70° C.	90° C.
0.5	2	0.129	0.122	0.117
0.5	3	.159	.144	.138
0.5	4	.171	.153	.142
0.5	5	.162	.153	.141
0.5	6	.142	.146	.138
1.0	2	.140	.138	.135
1.0	3	.169	.176	.170
1.0	4	.184	.184	.178
1.0	5	.181	.182	.176
1.0	6	.162	.175	.172
1.5	3	.163	.176	.165
1.5	4	.197	.187	.177
1.5	5	.210	.204	.184
1.5	6	.216	.209	.188
2.0	4	.202	.218	.178
2.0	5	.247	.218	.178
2.0	6	.283	.248	.196

If the table of hydrogen ion concentrations published in a previous paper (2) is referred to, it will be seen that the variation in hydrogen ion concentration is about 100 times that of bisulphite ion concentration. The system calcium-oxide–sulphur-dioxide–water is a true buffer solution as far as bisulphite ions are concerned.

Consequently since the bisulphite ion concentration varies only slightly with change in temperature, the concentration of the hydrogen ion probably governs the precipitation. It is easily understood then why a relatively small rise in temperature causes the formation of a heavy precipitate, as it has been shown that the decrease in hydrogen ion concentration with rise in temperature is relatively large. Hence, as the temperature rises, a critical hydrogen ion concentration is reached at which precipitation starts, and, as the hydrogen ion concentration falls rapidly with further rise in temperature, the precipitate continues to form rapidly.

In conclusion it is worth pointing out that Table IV, showing bisulphite ion concentrations, is of considerable interest. The relative constancy of bisulphite ion concentration over a large range of temperature and concentration may well be of importance in connection with the mechanism of the delignification of wood. This will be discussed in a later paper.

The mechanism of precipitation can be used to explain the sudden increase in vapor pressure and decrease in conductivity at the precipitation temperature. When calcium sulphite is formed, sulphurous acid is liberated. This will displace the equilibrium in the direction of free sulphur dioxide, and this will result in an increase in pressure. On the other hand, a part of the sulphurous acid will ionize, and this will tend to increase the conductivity. Precipitation temperatures are usually high; therefore this tendency will be slight and will be much more than offset by the decrease in total ionic concentration caused by the removal of calcium as calcium sulphite.

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THE SORPTION OF LIME BY CELLULOSE AND WOOD[1]

By G. L. Larocque[2] and O. Maass[3]

Abstract

The adsorption of lime on cellulose and wood has been measured. On the basis of molecular proportions, the magnitude of the adsorption is shown to be much greater than that of sodium hydroxide. It is found that considerable time is required for saturation adsorption to take place. The adsorption on similar wood species is shown to be the same and much greater than on cotton cellulose.

Introduction

The sorption of sodium hydroxide by cellulose and the accompanying phenomenon of swelling or mercerization are established facts of long standing. Subsequently all the strong hydroxides, as well as the alkaline earth hydroxides, were found to be strongly absorbed, with or without a simultaneous swelling process.

No exact information is available in the literature on the absorption of calcium hydroxide on cellulose. All the hydroxides previously examined have monovalent ions, and it was therefore thought to be of special interest to determine the rate and magnitude of the sorption that takes place with lime solutions.

The method consisted in making ash determinations on samples that had been kept immersed and shaken in solutions of known concentration for definite lengths of time. A previous investigation (1) of the exact concentration of saturated lime solutions at various temperatures was a necessary prerequisite to the present investigation.

Experimental Method

In the present investigation, unsaturated solutions of lime are automatically brought into contact with the cellulosic sample at a temperature such that the solubility curve shows that precipitation on the fibre is impossible. In this manner, the difficulty of fixing the solubility in the liquid phase is overcome by a proper adjustment of the temperature in a specially constructed cell.

This cell is illustrated in Fig. 1, and consists of a $1\frac{1}{2}$ by 8 in. test tube, divided into an upper and a lower section by a perforated silver plate, which is suspended by two glass rods. The solution in the lower compartment is kept saturated by means of fragments of lime enclosed in a thick canvas bag. This bag is suspended by means of another vertical glass rod which is hinged at its upper extremity and is capable of a swinging motion from side to side,

as the test tube is rocked about a horizontal axis, by means of a motor-driven eccentric arrangement which is not shown in the illustration. The lower part of the test tube is immersed in a water bath, the temperature of which is maintained at 30° C. by means of a thermostat. Convection currents carry the saturated solution through the silver plate and into the upper part of the cell, which is kept 1° to 2° cooler by a cooling coil wound around the outside of the test tube.

Since the solubility of lime increases with lowering of the temperature, the solution in the upper compartment is thus kept unsaturated, but at a constant concentration for that temperature. Sorption from this solution takes place on the sample, which is hung in the upper compartment by means of a silver wire.
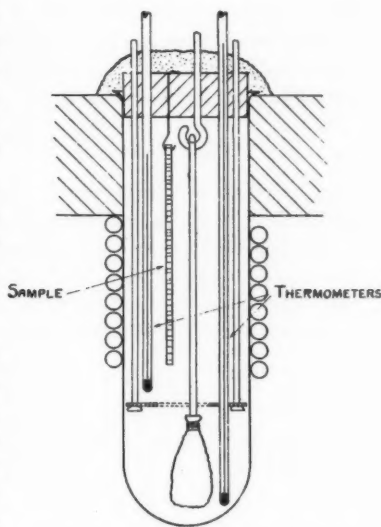

FIG. 1. *Calcium hydroxide sorption cell.*

Procedure

Wood flakes of black spruce, clean absorbent cotton, and absorbent cotton that had been previously treated for 80 hr. with 1% sodium hydroxide, acidified with 1% acetic acid and washed, were the three cellulosic materials that were employed.

The wood flakes were prepared from well seasoned wood by cutting thin slices with a circular saw, in a direction perpendicular to the transverse axis of the material. They were roughly 2.5 by 5 cm., and 2 mm. thick, and weighed approximately 2 gm. each. In this manner the wood cells (which average 3 mm. in length) were cut at least once along their length, so that the cell-structure of the wood offered no hindrance to the penetration of the alkali.

The wood samples were oven dried for eight hours at 105° C. A sample was then weighed, watersoaked by repeated evacuation and immersion in water, placed in the cell and allowed to remain there from ½ to 72 hr.

After the sample had been removed from the test tube, it was pressed for a few moments between filter papers, and immediately weighed. The difference between this and the original dry weight gave the weight of solution mechanically held. The concentration of the solution used being known from the temperature, a correction could then be made for the amount of lime in the liquid mechanically held by the sample.

The flake was then broken up, put into a porcelain crucible and ignited until no specks of carbon remained. The crucible was cooled in a desiccator in an atmosphere free from moisture and carbon dioxide, and weighed. From

this result, the ash adsorbed on the sample was calculated as a percentage of the dry sample weight. A temperature of 30° C. was used in the lower cell compartment. This corresponded to a saturation concentration of 1.23 gm. of calcium oxide per litre, or 0.022 molar (1).

Results

An adsorption isotherm of conventional shape was obtained, and the magnitude of the sorption, expressed in percentage of calcium oxide per gram of dry sample, is shown plotted on a time basis in Fig. 2. Saturation sorption
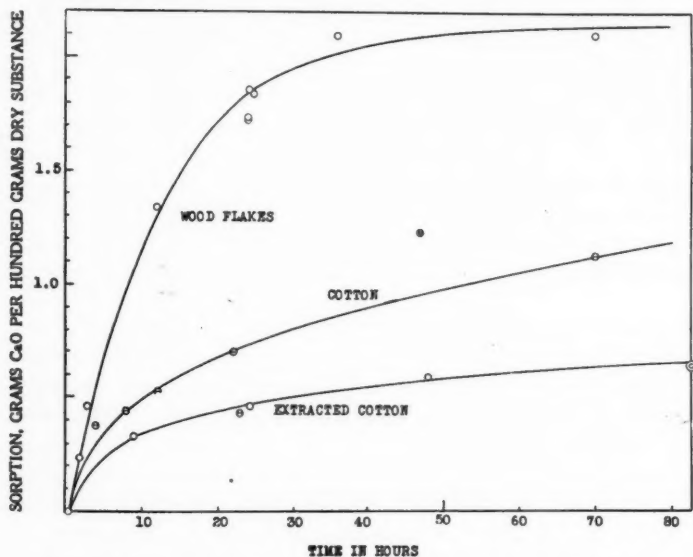

FIG. 2. *Calcium hydroxide sorption from 0.0219 molar solution at 28° C.*

values were obtained in 24 to 48 hr., and the maximum sorption was found to be 2.1% for the wood flakes, 0.6% for the extracted and approximately 1.2% for the unextracted cotton.

Discussion

For wood the sorption value at saturation is 3.74 millimoles of calcium hydroxide per gram of wood. At the same molar concentration the sorption of sodium hydroxide is about 0.3 millimoles per gram of wood (2). The greater adsorption of calcium hydroxide is in accordance with the increase in magnitude of adsorption that has been generally observed with ions of higher valency.

Cotton that had not been extracted with 1% sodium hydroxide gave erratic sorption values, probably because of lack of homogeneity in the material.

The sorption of lime on extracted cotton is less than it is on wood.   This is similar to the behavior with sodium hydroxide, where a greater adsorption was observed (2) for wood than for cotton cellulose at these concentrations. Furthermore, the wood structure is without effect, since identical sorption values were obtained for heartwood and sapwood specimens.   Identical sorption values were also observed for the two different species, black and white spruce.

The results are of considerable interest in connection with pulp and paper problems.   They draw attention to the existence of the phenomenon of adsorption in wood-alkali systems, and support the theory, which will be put forth in a subsequent paper, that adsorption is an important factor in determining the mechanism of commercial delignification reactions for the preparation of wood pulp.

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THE VISCOSITIES OF DEUTERIUM-HYDROGEN MIXTURES[1]

By A. B. Van Cleave[2] and O. Maass[3]

Abstract

A more intensive investigation than that previously reported by the authors has been carried out on the viscosities of dueterium-hydrogen mixtures at 22° C.

Deuterium prepared from a 99.5% sample of deuterium oxide was used. The results show that, within experimental error, the diameters of the D_2, HD and H_2 molecules are identical. Variations of the viscosity of some of the mixtures with the temperature were measured at −78.5° and −183.4° C. It was shown that Jeans' temperature-viscosity relation holds approximately for the mixtures. A comparison has been made of the various equations that have been suggested as expressing the relation between the viscosity of a gaseous mixture and the viscosities of its components.

Introduction

In previous publications (9, 10) the authors gave results of measurements of the viscosity and thermal conductivity of deuterium and some deuterium-hydrogen mixtures which indicated that the hydrogen isotopes have the same molecular diameter. This research supplies additional evidence for the above observation.

Material

The present sample of deuterium was prepared (9, 10) from 1 gm. of 99.5% deuterium oxide (sp. gr. 1.1073) purchased from the Ohio Chemical and Manufacturing Company. Using the well known equilibrium constant (5, 7), it was calculated that the final sample consisted of 98.01 molecular per cent of D_2, 1.98 molecular per cent of HD and 0.01 molecular per cent of H_2. Hence, a much purer sample of D_2 than that formerly used (9) was obtained. On a basis of atomic percentages the sample consisted of 99% deuterium and 1% of hydrogen. For details of experimental procedure the reader is referred to earlier papers by the authors. The experimental technique in preparing the deuterium has been fully described in the previous paper (9). On account of the high atomic percentage of deuterium oxide in the sample of deuterium oxide used, any value of the equilibrium constant at any temperature may be used without altering the calculated percentages by more than 0.01%.

Results

Table I shows the results obtained for the viscosity of the original sample and a number of deuterium-hydrogen mixtures at three different temperatures. Each value is the mean of three or four independent determinations.

The results in Table I are shown graphically in Figs. 1 and 2. Fig. 1 gives the curves for the variation of viscosity with temperature for each concentration used. The curves for 96% deuterium and 100% hydrogen are those given in the previous paper (9). Fig. 2 shows the variation of viscosity

TABLE I

VARIATION OF VISCOSITY WITH CONCENTRATION AND TEMPERATURE

Molecular per cent of deuterium	99.00	95.72	90.03	78.29	50.44	25.91	00.00
Temp., ° C.	Viscosity in C.G.S. units $\times 10^7$						
22	1238.8	1230.9	1213.3	1185.0	1081.0	988.0	878.8
−78.5	—	—	—	883.1	810.1	739.6	—
−183.4	—	—	—	497.8	460.1	423.3	379.3

with concentration for each of the three temperatures at which measurements were made. The 22° C. curve is the same as that previously given (9), with additional data obtained in the present work.

Discussion

The 22° C. curve in Fig. 2 indicates that the viscosity of deuterium-hydrogen mixtures is independent of the small number of HD molecules present, and that it depends entirely on the atomic percentages of deuterium and hydrogen present. For example, the 98 weight per cent deuterium used in the first investigation (9) contained 92.35% D_2, 7.45% HD and 0.20% H_2, assuming the equilibrium constant to be equal to 3, and had a viscosity at 22° C. of
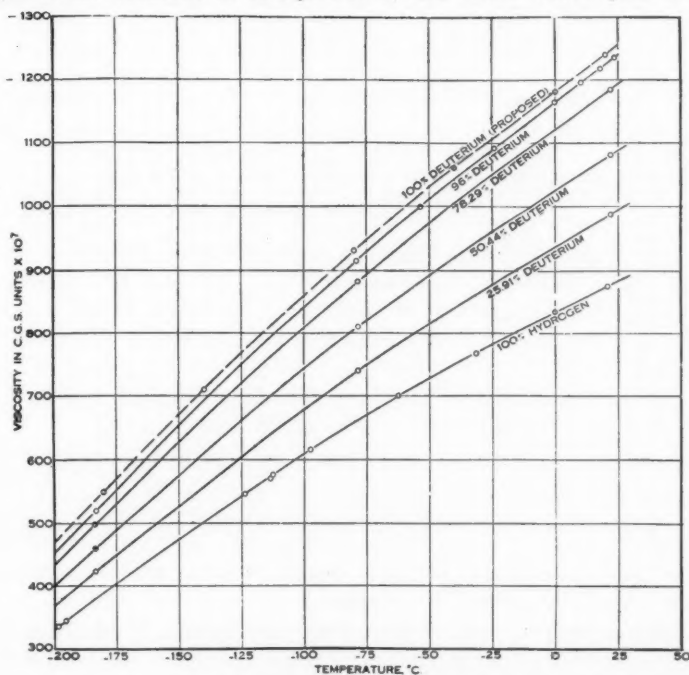

FIG. 1. *Variation of viscosity with temperature for various concentrations.*
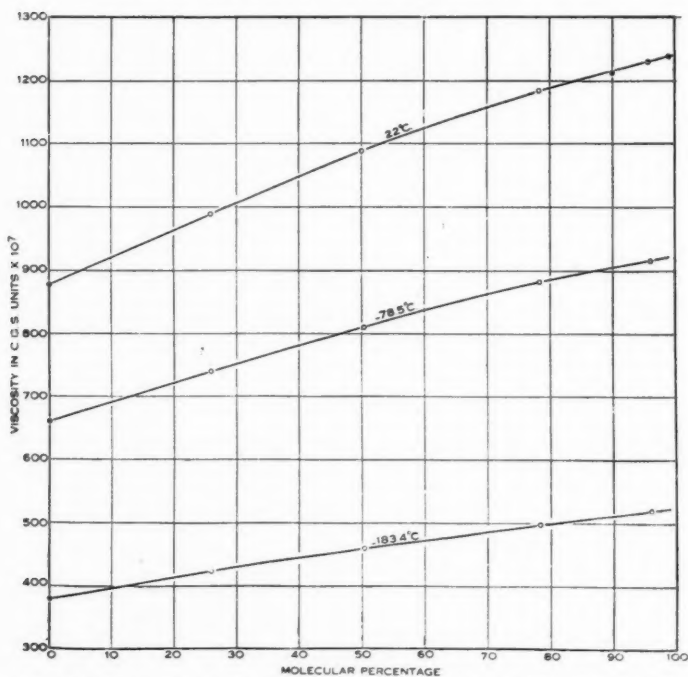
FIG. 2.   *Variation of viscosity with concentration for three different temperatures.*

1231.0×10^{-7} C.G.S. units, whereas an approximately 98 weight per cent deuterium sample, made by diluting the present sample with pure H_2, contained 94.76% D_2, 1.93% HD and 3.31% H_2, and had a viscosity at 22° C. of 1230.9×10^{-7} C.G.S. units.   This shows that the amount of HD present in the samples used in this and the previous work could properly be neglected, and the sample considered as being made up of D_2 and H_2 molecules alone. Such a result could follow only if the molecular diameters of D_2, HD and H_2 molecules are the same.   Thus the authors were justified in the extrapolation of the deuterium-hydrogen curve in Fig. 3 of the previous paper (9) to 100% deuterium, as this extrapolation passes directly through the point obtained for the viscosity of 99 mole per cent D_2 in the present work.

The curves in Fig. 1 are all very similar and each may best be represented by the equation proposed by Jeans, $\eta/\eta_o = (T/T_o)^n$, where n is approximately 0.699. However, at low temperatures the deviations from this relation became quite marked. As previously pointed out (9), none of the existing relations for the variation of the viscosity of gases with temperature are adequate over a large temperature range.

For the purposes of this discussion all the following calculations on the viscosity of D_2–H_2 mixtures have been made on the basis that the mixture consisted only of D_2 and H_2 molecules.   That is, the percentage of HD

molecules present in the original sample has been neglected. All calculations are based on the results obtained at 22° C., as not enough points were obtained at low temperatures to make a rigid test of the proposed expressions.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED RESULTS FOR THE VISCOSITY OF DEUTERIUM-HYDROGEN MIXTURES AT 22° C.

P_D atm.	P_H atm.	$\eta \times 10^7$, obs. C.G.S. units	$\eta \times 10^7$, calcd. by Puluj's method	% Dev.	$\eta \times 10^7$, calcd. by Suther-land-Thiessen method	% Dev.	$\eta \times 10^7$, calcd. by Trautz's method	% Dev.	$\eta \times 10^7$, calcd. by Chap-man's method	% Dev.
1.0000	0.0000	1242.5	1242.5	0.00	1242.5	0.00	1242.5	0.00	1242.5	0.00
0.9900	0.0100	1238.8	1239.4	0.05	1240.4	0.13	1239.9	0.10	1239.9	0.10
0.9608	0.0392	1231.0	1230.3	0.06	1232.1	0.08	1232.5	0.12	1232.1	0.08
0.9572	0.0428	1230.9	1229.1	0.15	1231.9	0.08	1231.6	0.06	1231.1	0.02
0.9111	0.0889	1217.0	1214.6	0.20	1218.6	0.13	1219.1	0.18	1218.8	0.15
0.9003	0.0997	1213.3	1211.1	0.18	1215.6	0.19	1216.1	0.22	1215.6	0.39
0.8677	0.1323	1205.0	1200.7	0.36	1206.3	0.10	1207.1	0.17	1206.6	0.13
0.7829	0.2171	1185.0	1173.1	1.00	1180.8	0.40	1182.4	0.22	1181.9	0.26
0.7634	0.2366	1174.3	1166.7	0.69	1175.7	0.12	1176.4	0.18	1175.9	0.14
0.6513	0.3487	1138.2	1129.0	0.82	1139.4	0.09	1040.8	0.25	1137.8	0.04
0.4998	0.5002	1088.2	1076.4	1.09	1086.7	0.14	1088.3	0.00	1088.4	0.02
0.2591	0.7409	988.0	985.7	0.23	991.2	0.32	994.3	0.63	995.1	0.61
0.2564	0.7436	991.3	984.7	0.66	989.9	0.14	993.1	0.18	993.9	0.26
0.0000	1.0000	878.8	878.8	0.00	878.8	0.00	878.8	0.00	878.8	0.00

Now that it has been conclusively shown that, considered from the point of view of viscosity measurements, the cross sections of deuterium and hydrogen molecules are the same, the approximation that it is necessary to make in some expressions for the viscosity of gas mixtures containing molecules of unequal diameter is here unnecessary.

The first equation to be tested was that of Puluj (2), as it contains no calculated constants. The fact that D_2 and H_2 molecules have the same molecular diameter causes Puluj's equation to reduce to the very simple expression $\eta_m = \eta_D (P_D + 0.5 P_H)^{\frac{1}{2}}$, where η_m is the viscosity of the gas mixture, η_D the viscosity of pure D_2, and P_D and P_H are the partial pressures of deuterium and hydrogen respectively. Thus if η_D is known, η_m may be calculated and *vice versa*. A comparison of the values calculated from this expression and those experimentally found is given in Table II. Values calculated from the empirical equation of Sutherland (3) and Theisen (4) are also included in the table. The constants of this equation were calculated from the experimental results for 3:1 and 1:3 mixtures of D_2 and H_2. The completed equation is

$$\eta_m = \frac{\eta_D}{1 + 0.543 \, P_H/P_D} + \frac{\eta_H}{1 + 2.123 \, P_D/P_H} .$$

Table II shows that Puluj's equation closely follows the experimental results for mixtures containing more than 86 molecular per cent of deuterium. Thus the interpolation previously made (9) in connection with the determination

of the molecular diameter of deuterium should be correct to within the error assigned. The empirical relation of Sutherland and Theisen represents, well within the experimental error, the experimental results over the whole concentration range.

The present results are of particular interest when applied to the expression proposed by Trautz (6), as no assumptions have to be made in regard to the molecular diameters of the components. This expression is

$$\eta_m = \frac{\eta_1 q_1^2 x^2 + 2\eta_{1 \cdot 2}\, q_{1 \cdot 2}^2 x(1-x) + \eta_2 q_2^2 (1-x)^2}{q_1^2 x^2 + 2q_{1 \cdot 2}^2 x(1-x) + q_2^2 (1-x)^2}\;.$$

For the deuterium-hydrogen system, $q_1 = q_{1 \cdot 2} = q_2$ (the molecular diameter) and the above equation reduces to

$$\eta_m = \eta_D P_D^2 + 2\eta_{1 \cdot 2} P_D P_H + \eta_H P_H^2$$

where we have written η_D and η_H for η_1 and η_2, and P_D and P_H for x and $1-x$ respectively; $\eta_{1 \cdot 2}$ is a constant.

Trautz (6) has given methods of evaluating the constant $\eta_{1 \cdot 2}$, but when one such calculation was tried with the present results a value of $\eta_{1 \cdot 2}$ that was much too high was obtained. Hence it was decided to treat Trautz's equation in a purely empirical manner, that is, to evaluate $\eta_{1 \cdot 2}$ from the experimental results for the 50% mixture. The value of $\eta_{1 \cdot 2}$ obtained was 1116×10^{-7}. Hence the completed equation becomes

$$\eta_m = \eta_D P_D^2 + 2232 + 10^{-7}\, P_D P_H + \eta_H P_H^2\;.$$

Values calculated from this equation, together with those calculated from Chapman's equation, are also compared with the experimental values in Table II.

The theoretical equation of Chapman (1) is

$$\eta_m = \frac{E P_D^2 + F P_D P_H + G P_H^2}{E P_D^2/\eta_D + F_1 P_D P_H + G P_H^2/\eta_H}\;,$$

where E, F, F_1 and G are calculated constants (1).

Since the constants F and F_1 depend on the diffusion coefficient $D_{1 \cdot 2}$, it was necessary to make a calculation using the following formula (1)

$$D_{1 \cdot 2} = 1.34\,(P_D\, \eta_D/\rho_D + P_H\, \eta_H/\rho_H)\;,$$

where ρ_D and ρ_H are the densities of D_2 and H_2 respectively. The value of $D_{1 \cdot 2}$ calculated in this manner was 1.208. By methods of trial and error it was found that the best value of k is 0.647 (1). Proceeding in the manner indicated by Chapman the values of the constants were found to be— $E = 2.294$, $F = 3.633$, $G = 1.324$ and $F_1 = 3.309 \times 10^4$. These constants were used in calculating the values given in Table II.

The equations of Chapman and Trautz (1, 6) agree very well with the experimental results. The theoretical equation of Chapman represents the present results particularly well. This also seems to indicate that the error introduced by disregarding the percentage of HD molecules in the mixture is small.

The main interest in making comparisons of the viscosity-mixture equations of deuterium-hydrogen mixtures lies in the fact that the molecules concerned are of equal diameter but different weight. It is thus possible to effect certain simplifications, such as putting $q_1 = q_{1\cdot2} = q_2$, etc.

The system deuterium-helium is to be investigated next, as in this one the molecules are of virtually identical weight but of different diameters.

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